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The effect of secondary hardening on the notch toughness of molybdenum alloyed steel

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THE EFFECT OF SECONDARY HARDENING ON THE NOTCH TOUGHNESS OF MOLYBDENUM ALLOYED STEEL

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ABSTRACT

The effect of secondary hardness on the notch toughness of a medium carbon steel alloyed with molybdenum was investigated. The hardness response for the base 0.42 carbon steel with 0% molybdenum, with 2% molybdenum, and with 5% molybdenum was first measured at varying tempering temperatures. From this data tempering temperatures were selected and applied to individual series of Charpy V-notch impact specimens. After testing the resultant transition temperature responses were correlated with the hardness responses for the various heat treat conditions. The results indicated that the heat treatment required to produce the maximum secondary hardness response did not produce the maximum loss of notch toughness. Molybdenum additions appeared to shift the overall transition temperature response to higher tempering temperatures thereby delaying the onset of temper embrittlement and extending the range of "500 degree embrittlement." The molybdenum additions employed did not appear to produce a significant reduction in the severity level of "500 degree embrittlement."

INTRODUCTION

As a result of the transition from liquid to solid fuels in many of the rocket and missile systems currently employed by the armed services, materials requirements for the missile bodies have undergone a drastic revision. In most liquid fuel systems light structural framework and thin skin panels provide the tankage for the fuel as well as the exterior skin of the missile. In solid fuel systems, however, the fuel container also doubles as a combustion chamber. The motor case must now be capable, therefore, of containing and channeling the extreme heat and gas pressure built up by the combustion reaction plus withstanding the erosive effects of the reaction products. The case must also be capable of sustaining the forces induced during firing, forces caused by the maneuvering of the missile, plus the normal storage and handling shocks.

One family of steels that evoked the early interest of solid fuel motor case designers was that group referred to as the "hot work tool steels." Some typical examples of these steels, as classified by the American Iron and Steel Institute, are the chromium alloyed types such as H-11, the tungsten alloyed types such as H-21, and the molybdenum alloyed types such as H-41[1]. Considerable data exists indicating that these hot work tool steels are capable of developing high hardness values, Rockwell C 50 and above, and high tensile properties, 180,000 psi to

greater than 200,000 psi tensile strengths, at temperatures ranging from 900°F to 1100°F[2]. The high strength and hardness values of the hot work tool steels at elevated temperatures are the result of the phenomenon identified as secondary hardening. Secondary hardening is manifested in alloy steels by a delay in the softening of the tempered martensite structure in the temperature range from 600°F to 1200°F. In those alloy steels which show a pronounced secondary hardening effect, a complete reversal in the slope of the hardness versus tempering temperature curve occurs forming a distinct hardness peak generally at temperatures between 1000°F and 1150°F[2,3]. Considerable work has been performed on the actual mechanism of the secondary hardening reaction and most workers now ascribe its occurrence to the coherent precipitation of various alloy carbides[2,3,4,5,6].

The transformation of retained austenite has also been shown to have a retarding effect on the softening of martensitic steels during tempering[2,7]. Crafts and Lamont[5] have pointed out, however, that this transformation is not essential to the secondary hardening reaction; it is more properly relegated to the position of a complicating factor in any study of the secondary hardening phenomenon.

Very little published data exists on the notch toughness properties of the hot work tool steels. The majority of the limited data that does exist is based upon room temperature Charpy "V" notch and unnotched Izod specimens[2]. Extensive literature

searching has failed to disclose any notch toughness data based upon the transition temperature behavior of these steels as measured by readily understood tests. This investigation was initiated to study the notch toughness, as indicated by the brittle to ductile transition temperature behavior, of alloy steels subject to secondary hardening. The necessity of separating variables precluded the use of the more complex commercial alloys which utilize two or more strong carbide forming elements. It was decided to rely upon one principal alloy addition which would produce a distinct secondary hardening reaction. From the several elements available, molybdenum was selected since it also decreases the rate of temper embrittlement in alloy steels[8]. The relationship between secondary hardening and temper embrittlement could not be ascertained from the literature and consequently the minimization of any extraneous embrittling reactions was desired. By incorporating alloys with varying molybdenum content plus the selected utilization of the appropriate range of tempering temperatures the secondary hardening response could be determined and correlated with any consequent effects on the notch toughness properties.

In order to minimize complications with retained austenite a carbon level of approximately 0.40-0.45% was selected and the manganese content reduced to a level sufficient only to provide some workability in the ingot breakdown. Further control on the level of retained austenite was obtained by the use of a liquid nitrogen quench following all austenitization treatments.

EXPERIMENTAL PROCEDURE

General

The initial experimentation performed in this program was the determination of the optimum austenitizing temperature for each investigated alloy. The temperature producing the peak as-quenched hardness value after one hour at temperature was utilized as the optimum temperature. Following this determination the hardness response for each alloy as influenced by the tempering temperature was measured. Based on these hardness results, heat treatments were selected and performed on individual series of Charpy V-notch impact specimens. After impact testing the transition temperature responses for the investigated alloys were determined and compared with the hardness behavior over a range of tempering temperatures to determine the influence of secondary hardening on the notch toughness.

Raw Materials

Three one hundred pound heats were air induction melted for this investigation. The molybdenum contents for the three heats were targeted at 0%, 2%, and 5%. Deoxidation was accomplished by silicon additions to the ladle. The final analyses of the three heats are presented in Table I.

The forging practice used to break down the as-cast ingots depended upon the alloy content. The 0% molybdenum base alloy was forged at 2200°F with finishing at 1800°F. The 2% and 5%

molybdenum alloys were forged at 2050°F with finishing at 1800°F. Reheat was used as required. The final forged product consisted of hexagonal cross section rods approximately 3 feet in length and 5/8ths of an inch in diameter.

Preparation of Specimens

For determining the optimum austenitizing temperatures and the hardness behavior as influenced by the tempering temperature, individual hardness specimens were cut to length from the rough stock on a water cooled radial cutoff saw. Three quarter inch long slugs were used for the former and two and one quarter inch long slugs for the latter. After the austenitization and quench two cross sectional faces were carefully ground with a wet belt at opposite ends of each austenitizing temperature slug to provide a smooth and parallel measuring surface. The longer hardness response slugs were cross sectioned at their longitudinal mid-points after the completion of the austenitizing and tempering treatments. An internal face and the companion end face were then carefully ground on a wet belt to provide a parallel measuring surface. (Hardness impressions for the longer specimens were taken on the internal face).

Charpy specimens were prepared by first machining oversize blanks from annealed stock to a cross section of 0.440 inches square and an approximate length of 2.3 inches. Following the austenitizing and tempering treatments the oversize blanks were

finish ground to size, 0.394 inches on side, cut to length on a water cooled radial cutoff saw, and notched in a thread grinder with a self dressing diamond "trueing" device. Periodic optical comparator checks were made on the finish machined impact bars to insure that the prescribed notch geometry was maintained.

Specimens for metallographic study, x-ray diffraction investigations, and hardness corroboration were cut from rough machined Charpy blanks and fractured impact bars representing each separate heat treat or test series. These specimens were primarily cross sectional faces carefully cut at the longitudinal midpoint or immediately adjacent to the notch with a water cooled radial cutoff saw. Necessary surface preparation was again performed on a wet belt.

Heat Treatment

With the exception of the stock used in the initial determination of the austenitizing temperatures, all materials used for hardness and impact specimens received an annealing treatment. The stock for annealing was cut into one foot lengths, packed into a cylindrical retort, and surrounded by a mixture of spent carburizer and coke breeze. The retort was then capped and loaded into a recirculating air furnace where it was held at the annealing temperature for one hour and then furnace cooled until it was below 900°F. The retort was then removed from the furnace and air cooled to room temperature. The

furnace cool required a minimum of fifteen hours. Periodic temperature monitoring was performed during the anneal with chromel-alumel thermocouples inserted into the retort.

The austenitization treatments for the 0% Mo alloy were performed in molten salt. Specimens were held at temperature for one hour. A variety of temperatures were initially investigated and 1540°F was selected as the optimum austenitizing temperature, see Figure 1. This temperature is slightly higher than the peak of the as-quenched hardness curve in order to insure complete hardenability.

The 2% Mo alloy was austenitized at various temperatures for one hour in either high temperature salt or a recirculating air furnace. In the latter case, specimens were packed in a carburizing boat and surrounded by a mixture of spent carburizer and coke breeze. Two austenitizing temperatures were selected from the above survey: 1645°F, cf. Figure 1, which produced an average ASTM Fracture Grain Size of eight; and 2100°F which produced an average ASTM Fracture Grain Size of five to six. The lower austenitizing temperature treatments were performed in the salt bath; the higher, in the recirculating air furnace.

The austenitization treatments for the 5% Mo alloy were handled in the same manner as the high temperature austenitizing treatment for the 2% Mo alloy. A temperature of 2150°F was selected as the optimum temperature, see Figure 2. A higher austenitizing temperature for this alloy was considered prohibitive since an extrapolation of Bain's data[9] indicated

that the liquidous occurred at approximately 2200°F.

Austenitization was terminated for the three alloys by an intermediate quench into brine for the 0% Mo alloy and oil for the 2% and 5% Mo alloys. Immediately following the intermediate quench all samples were given a final quench in liquid nitrogen and held at that temperature for a minimum of ten minutes.

Tempering treatments for all specimens were performed in a recirculating air tempering furnace. With the exception of the series noted below all specimens were held at temperature for one hour and then brine quenched from the tempering temperature. Three series of impact specimens from the 2% Mo alloy were given a double tempering treatment following their austenitization and quench cycle. These series were tempered for one hour at a selected temperature and then quenched into brine, immediately followed by a quench into liquid nitrogen. The specimens were again held for a minimum of ten minutes at -320°F. The second temper was performed at a temperature fifty Fahrenheit degrees below the first temper for a period of one hour. The only quench from the second temper was into brine.

Throughout all austenitizing and tempering treatments periodic temperature monitoring was performed with chromel-alumel thermocouples in direct contact with the specimens. The specific variables involved in the heat treating of the various specimens are enumerated in the tabulated results, refer to Tables II, III, and IV.

Testing

All hardness tests were performed on a Wilson-Rockwell testing machine. The accuracy of the machine was checked with standard test blocks prior to the testing of any experimental specimens. The hardness data developed during the determination of the optimum austenitizing temperatures, and the hardness responses as affected by the tempering temperatures were all derived from a five reading traverse conducted across the prepared surface of each test specimen. The individual readings were averaged to provide a hardness data point corresponding to the particular heat treatment. In addition to the regular hardness specimens, readings were also made on cross sectional specimens cut adjacent to the fracture surface on Charpy bars from each heat treated impact series. These hardness readings corroborated the effectiveness of heat treatment and insured correspondence with the original hardness versus tempering temperature data.

Impact testing was carried out on a Tinius Olsen 220 foot pound capacity impact testing machine. A fully heat treated and finish machined series of Charpy V-notch specimens normally consisted of fourteen bars. Each series was tested through a range of test temperatures and the absorbed energy recorded for each fractured bar. A graph of fracture energy absorbed versus testing temperature was then plotted. The plots produced a family of curves for each alloy. Representative samples of these curves are shown in Figure 3.

The low impact testing temperatures were obtained by immersing the impact specimens in baths of either liquid nitrogen and methyl butane, or dry ice and alcohol. Testing temperatures above room temperature were obtained by immersing the specimens in baths of heated oil. Temperature monitoring was performed in the baths with either copper constantan or chromel-alumel thermocouples placed at the notch region on each test specimen. Once the temperature of the test specimen had stabilized at the desired testing temperature the specimen was rapidly transferred to the impact machine anvil with tongs, which had also been immersed in the same bath. Handling time between the bath and hammer impact averaged approximately three seconds.

From the fracture energy-testing temperature curves representing each impact test series, temperatures were picked off corresponding to a prescribed level of absorbed energy. These particular energy levels were determined by an analysis of the spread of values of impact energies obtained for all series tested. The diversity in the amount of energy absorbed between the three alloys over the range of tempering temperatures used necessitated the selection of both a six and a ten foot pound criterion. These two criteria provided the greatest continuity and ease of comparison between all variables. The temperatures corresponding to the selected energy levels are identified as the transition temperature for the particular energy criterion. The shift in these temperatures

from series to series is utilized to show the influence of alloy content, tempering temperature, and austenitic grain size on the ability of the Charpy bar to absorb impact energy.

Metallographic testing performed during the course of this investigation included microstructural examinations of representative samples from each heat treat condition, including the as-forged condition, and process control specimens from each heat treat cycle. The specimens were primarily cross sectional surfaces cut adjacent to the notch on finish machined impact bars or at the longitudinal mid-point on impact blanks and rough forged slugs. Specimen preparation was performed according to standard metallographic hand polishing techniques[10]. The etchants found to be the most successful for the alloys involved were solutions of one per cent nital, picral, or mixtures of the two solutions. The average etching time was approximately ten seconds.

Fracture surfaces from broken impact bars representing the various austenitizing conditions were compared with ASTM Fracture Grain Size Standards to determine the prior austenitic grain sizes.

Studies were also made on representative samples from the various austenitizing treatments to determine the quantities of retained austenite remaining after the quench to liquid nitrogen temperatures. Standard X-ray diffraction techniques were utilized on these determinations[11].

RESULTS

The hardness responses of the three alloys as influenced by the tempering temperature are individually plotted in Figures 4, 5, and 6; and grouped as a composite plot in Figure 7. The data points are tabulated in Tables II, III, and IV.

With first consideration directed to the hardness response of the 0% Mo or base alloy, it can be seen from Figure 4 that the behavior is quite straightforward and agrees well with published data for a water quenched AISI 1040 steel[12]. It is apparent that this alloy is not susceptible to a secondary hardening reaction.

The 2% Mo alloy on the other hand is clearly undergoing a secondary hardening reaction with a peak in hardness occurring in the neighborhood of 1050°F, refer to Figure 5. Good agreement exists between the hardness specimens used specifically for determining the hardening response and the readings taken from sectioned Charpy bars representing each heat treated impact series. The configuration and level of response of the experimentally determined curve agrees well with the data of Bain and Paxton for a 0.35 carbon steel containing 2% molybdenum[13]. The three double temper data points shown on the plot appear to indicate a slight vertical shift from the curve as determined by the single temper specimens. Figure 5 also shows that if the austenitizing temperature is raised from 1645°F to 2100°F a small vertical displacement in the tempering curve will appear.

During the preparation of the specimens it was noted that the as-forged stock from the 5% Mo alloy had a heavy concentration of forging bursts along the center axis of the rods. By utilizing radiographic and physical cut-up inspection measures sufficient stock was salvaged from the alloy to provide a limited number of impact bars plus the specimens for the hardness versus tempering temperature investigation. Unfortunately this restriction was to markedly reduce the anticipated evaluation of the 5% Mo alloy. It became necessary, therefore, to rely primarily upon the the 2% Mo alloy for the investigation of the secondary hardening response with the 0% Mo alloy providing the base for comparison. The 5% Mo alloy was relegated to the position of providing data of only supporting value. The hardness data for the 5% Mo alloy is presented in Figure 6. A very distinct peak occurs in the range 1050°F to 1100°F. The agreement between the data points derived from the hardness specimens per se and the sectioned Charpy specimens representing each heat treated impact series is quite good. The scatter is approximately one point on the Rockwell C scale which is equivalent to that experienced with the 2% Mo alloy. The one double temper data point although slightly harder is still within the scatter band for the curve as determined by the single temper hardness data. A comparison of the single temper 5% Mo alloy data with Bain and Paxton's data for a 5% molybdenum addition to a 0.35 carbon steel[13] shows reasonable agreement with the exception that the experimental

curve is shifted to somewhat higher hardness values and the secondary hardening peak is more pronounced.

When the composite plot of the three hardness curves is considered, see Figure 7, the effect of the molybdenum additions on hardness is immediately apparent. Excluding for the moment the hardness of 2% Mo alloy at tempering temperatures below 400°F which will be discussed in a forthcoming section, the two alloys containing molybdenum both show an increase in their overall hardness level. Next, the drop-off in the hardness of the tempered martensite structure of the two molybdenum containing alloys is markedly retarded at increased tempering temperatures and completely reversed as the secondary hardening peak is approached. It is interesting to note that the temperature at which the maximum secondary hardening response is experienced does not undergo a noticeable shift when the molybdenum content is increased. An additional increase in the overall hardness level and the accentuation of the secondary hardness peak does occur, however, when the molybdenum content is raised from two to five per cent. Once the secondary hardness peak has been attained the drop-off in hardness for both molybdenum containing alloys is very rapid and their hardness levels tend to approach the 0% Mo alloy hardness at high tempering temperatures.

The transition temperature response of the 0% Mo alloy is plotted in Figure 8 for two fracture energy criteria. The hardness response is also included to facilitate correlation. The

six foot pound criterion curve indicates the presence of a plateau in the transition temperature range 500°F to 600°F. This plateau or higher level of transition temperature at low tempering temperatures is commonly referred to as "500 degree embrittlement"(14). At about 600°F the transition temperature falls off rather steeply, levels off near 800°F, and then starts a gradual increase with tempering temperatures of 900°F or higher. The ten foot pound criterion curve duplicates the six foot pound behavior although the data is not as complete at the lower tempering temperatures. When the transition temperature curves are compared to the hardness curve, the upper tempering temperature limit of the plateau appears to coincide with the point on the hardness curve where the drop-off in hardness assumes a linear character. No other correlations are evident.

The transition temperature response of the 2% Mo alloy shows a general similarity to that of the 0% Mo alloy, c.f. Figure 9. Both the six and ten foot pound energy criteria curves display a broad plateau of increased embrittlement in the 500°F to 700°F tempering range. At approximately 750°F, a rapid drop from the transition temperature plateau occurs. As with the 0% Mo alloy, the drop-off in transition temperature appears to bear a relationship to the inflection point on the hardness curve. After the initial rapid drop in transition temperature a gradual reduction in the slope of the curve occurs until a minima is reached. Little relationship appears to exist between the minima and the continued retardation in the softening of the tempered martensite. After

passing the minimal point the transition temperature response initiates a gradual rise with increasing tempering temperature. It should be noted that no discontinuous effects in the transition temperature response are apparent at or beyond the point of maximum secondary hardness.

Three double temper impact series data points are also included in Figure 9 for both fracture energy criteria. It is immediately apparent that double tempering produces a marked increase in the level of the transition temperature regardless of criteria or tempering temperature. This behavior is opposite to the drop in the transition temperature that would normally be expected to occur in highly alloyed steels which require double tempering to eliminate retained austenite. Each set of three points appears to parallel the response of the single temper curve for the respective energy criterion. The reader is reminded that little, if any, effect occurred in the hardness response as a result of the double tempering treatment.

The presence of a rapid drop-off from the plateau for the 2% Mo alloy shown in Figure 10 represents data from four series of impact bars austenitized at a temperature of 2100°F. This treatment produced a prior austenitic grain size of ASTM 5-6.(The data in Figure 9 represents the 2% Mo alloy austenitized at a temperature of 1645°F with a prior austenitic grain size of ASTM 8.) The drop-off point at the upper tempering temperature limit of the plateau still bears an apparent relationship to the inflection point in the hardness response for the higher austenitizing temperature.

Turning now to the transition temperature behavior of the 5% Mo alloy as it is plotted in Figure 11, it is evident from the data points that this alloy is subject to more scatter than previously experienced with the other two alloys. The transition temperature curve for the six foot pound energy criterion does show a behavioral similarity with that of the 2% Mo alloy in the tempering region covered, i.e. the area surrounding the minimal point. For reasons previously noted the data points do not cover a region of sufficient breadth to indicate the presence of a plateau or a rapid drop from this plateau as found in the 2% Mo alloy. One data point for a double tempered impact bar series is included in Figure 11. The point is within the heavy scatter band for this alloy and does not indicate any abnormality in the transition temperature response.

Two comparisons of the transition temperature response at the same impact energy criterion for the alloys and heat treatments investigated are presented in Figures 12 and 13. In order that the differences in the respective austenitizing temperatures and their consequent austenitic grain sizes are kept in mind the data is summarized in tabular form as follows:

Alloy	Austenitizing Temperature	Average ASTM Fracture Grain Size
0% Mo	1540°F	6
2% Mo	1645°F	8
2% Mo	2100°F	5-6
5% Mo	2075°F	5

The changes that the addition of molybdenum produces on the transition temperature of the base 0.40 carbon steel are more obvious in these two graphs. The most significant change is the extension of the transition temperature plateau to higher tempering temperatures. The addition of two per cent molybdenum extends the plateau by approximately 200 Fahrenheit degrees. On the vertical axis the level of the transition temperature is only slightly reduced, if at all, by the addition of the molybdenum to the base alloy. These assessments are based on a comparison of the two alloys with equivalent austenitic grain sizes, see the curves for the 0% Mo alloy and the 2% Mo alloy austenitized at 2100°F. Caution must be exercised when comparing the 0% Mo alloy and the 2% Mo alloy austenitized at 1645°F since a differential of two ASTM grain size numbers exists in the prior austenitic grain size. The effect of two ASTM grain size numbers apparently causes a vertical shift of approximately seventy-five degrees in the transition temperature and an extension of the plateau of increased transition temperature to higher tempering temperatures by approximately 100 degrees Fahrenheit, refer to the two 2% Mo curves.

Molybdenum additions also appear to induce a delay in the onset of temper embrittlement. The onset of temper embrittlement is taken to appear at the minimal point in the transition temperature curve. By extrapolating the transition temperature curve of the 2% Mo alloy austenitized at 2100°F in a manner parallel to that of the alloy austenitized at 1645°F and then comparing it with the 0% Mo alloy of equivalent grain size, it appears that temper embrittlement is delayed several hundred Fahrenheit degrees. Again it is pointed out that no discontinuities

occur in any of the curves in the tempering region associated with the secondary hardness peak (1050°F).

The six foot pound composite plot, Figure 13, also includes the limited transition temperature data for the 5% Mo alloy. This alloy is significantly more embrittled than either the 0% Mo or the 2% Mo alloys since even the minimum level of transition temperature for the 5% Mo alloy is either equivalent to or more severe than the maximum level of transition temperature for the other two alloys. Additional comments on this condition are included in the Discussion portion of this paper.

As noted in the Experimental Procedure, metallographic specimens from each alloy in the as-forged, annealed, fully hardened, and hardened and tempered conditions were examined for microstructure variations and as heat treat control specimens. The latter specimens were used primarily to determine the extent of any surface decarburization or carburization which occurred during the heat treatment. The maximum total plus partial decarburization observed did not exceed 0.013 inches and occurred on rough machined impact blanks which were austenitized at 2100°F. Since the rough machined Charpy blanks had 0.023 inches of excess stock per side, final machining operations more than compensated for any surface attack. The removal of the undesirable surface layer was verified with cross sections from finish machined bars.

The metallographic studies of the various structures produced during the heat treating phases of this investigation did not disclose any significant irregularities. Particular attention was paid to the quenched and tempered specimens and various etchants were applied in attempts to bring out the ferritic and prior austenitic grain sizes. Although these attempts were not successful with respect to the ferrite grain size, moderate success was achieved in bringing out some prior austenite grains. A series of photomicrographs for the three alloys in the hardened and tempered condition are incorporated as Figures 14 through 17. The partial delineation of prior austenitic grains can be observed in the low magnification photographs of Figures 14, 16, and 17.

The representative samples from each of the three alloys in the fully hardened (as-quenched) condition which were examined by X-ray diffraction techniques[11] for retained austenite developed the following data:

Alloy	Austenitizing Conditions	Retained Austenite
0% Mo	1540°F/1 hour/brine quench plus liquid nitrogen quench	0.54%
2% Mo	1645°F/1 hour/oil quench plus liquid nitrogen quench	1.04%
2% Mo	2100°F/1 hour/oil quench plus liquid nitrogen quench	1.74%
5% Mo	2075°F/1 hour/oil quench plus liquid nitrogen quench	2.35%

The level of retained austenite in all three alloys is considered to be relatively insignificant. The accuracy of determination is considered to be plus or minus one percent.

DISCUSSION

The hardness results of this investigation have indicated that additions of two and five percent molybdenum to a low manganese 0.40 carbon steel will induce a secondary hardening reaction after tempering for one hour. The secondary hardness peak occurs at a tempering temperature in the neighborhood of 1050°F. A displacement in the location of this secondary hardening peak to higher or lower tempering temperatures for these alloys does not occur as a consequence of altered austenitizing conditions or molybdenum content. This statement is premised on the lack of significant deviation between the peak of the 2% Mo alloy austenitized at 1645°F and that for the 5% Mo alloy austenitized at 2075°F. From the data of the 2% Mo alloy it appears that raising the austenitizing temperature will cause only a slight overall increase in hardening level per given tempering temperature. This increase in hardness with austenitizing temperature is undoubtedly the result of solid solution effects which occurred in the austenite.

The secondary hardness peak is believed to arise from the precipitation of the Mo_2C carbide. Both Kuo[15,16] and Irvine and Pickering[17] have found that the intermediate carbide which

appears after or coincidentally with cementite and is responsible for secondary hardening in molybdenum containing steels is of the form Mo_2C. This carbide is replaced after much longer times, or at higher tempering temperatures, by carbides of the form Mo_6C, $Mo_{23}C_6$, or an unresolved carbide identified as Mo_aC_b. Both sets of investigators identified the carbides by X-ray diffraction techniques on powders electrolytically extracted from the matrix. From a 0.42 carbon steel with 2.85 Mo, Kuo identified Fe_3C and Mo_2C after three minutes at 1300°F, and $Fe_3C + Mo_2C + Mo_aC_b$ after one hour at 1300°F. Only Mo_2C was identified in a 0.38 carbon steel with 5.15 Mo after three minutes or even after one hour at 1300°F.

Irvine and Pickering working with a bainitic matrix identified Mo_2C in a 0.10 carbon steel with 2.05 Mo after one hour at 1000°F and this carbide continued to exist beyond 1300°F. Carbides of the form $Mo_{23}C_6$; Mo_aC_b and MoC were not identified until tempering conditions corresponding to extensive overaging were utilized, i.e. tempering for one hour at a temperature in the neighborhood of 1400°F. (The experimental data of this investigation indicates that tempering at 1300°F for one hour is sufficient to induce overaging.)

Excellent data exists, therefore, to indicate the form of the carbide responsible for the secondary hardening peak as Mo_2C. The temperatures at which the effects of Mo_2C precipitation are felt, however, are still subject to the vagaries of the detection

technique. X-ray diffraction of electrolytically extracted carbide particles indicates that Mo_2C exists at temperatures in the neighborhood of 1000°F after one hour of tempering. It is apparent, however, that the Rockwell C hardness measurements have sensed this carbide not only at temperatures in the neighborhood of 1050°F, which corresponds to the secondary hardness peak, but at temperatures 400 or more Fahrenheit degrees below this temperature. Parameters of a more subtle nature may indicate the presence of the Mo_2C carbide at even lower temperatures, if it exists below 600°F.

The comparison of the hardness responses for the two molybdenum alloys indicated a substantial increase in hardness with increased alloy content. The increase in the overall hardness level and the accentuation of the secondary hardness peak between the 2% Mo and 5% Mo alloys is believed to be due in part to increased precipitation of the Mo_2C carbide. The effects of increased solid solution reaction should also be felt, especially at the lower tempering temperatures, since more molybdenum would be available and higher temperatures present to induce greater solubility and homogeneity in the original austenite.

Previous remarks in the Results concerning the three hardness responses on the composite plot, Figure 7, deferred discussion on the lower hardness of the 2% Mo alloy as compared to the 0% Mo alloy at tempering temperatures below 400°F. This condition

is believed to result from the metallographic preparation of the as-quenched samples. At room temperature the difference between the two curves is only on the order of two points on the Rockwell C scale and is based on two as-quenched samples, see Figures 5 and 7. Slight overheating during metallographic preparation is believed to have induced tempering effects. These same effects would be masked for specimens representing higher tempering temperatures. Retained austenite is not considered to be responsible for the condition, since the quantities identified by X-ray analysis are insignificant.

Before discussing the transition temperature results, it should be understood that the transition temperature has been used in this investigation as a measure of the embrittlement to which most alloy steels are subject. Since embrittlement is a relative term, it requires definition as to what is considered ductile or brittle behavior. In this particular investigation two impact energies have been selected as the limiting condition between ductile and brittle behavior, i.e. the six and ten foot pound impact energy criteria. The curves plotted in Figures 8 through 13 show, therefore, that the investigated alloys after being heat treated in a given manner will undergo a transition from ductile to brittle failure when impact tested at a specific temperature, further identified as the "transition temperature."

The transition temperature is not a constant value; it is a function of several variables. The variables of primary interest in this study were the molybdenum content and the tempering temperature.

The use of molybdenum as an alloying agent has produced some rather interesting effects on the transition temperature of the 0.40 carbon base alloy; in particular, the shift in the transition temperature plateau to higher tempering temperatures, and the delay in the onset of temper embrittlement to higher tempering temperatures Both of these effects may be the result of one general overall shift in the transition temperature response as opposed to two individual effects. Further investigation beyond the two extremes of the tempering region studied are required, however, to substantiate this possibility. The role of the molybdenum additions in these effects is not clear; however, the most logical presumption would be that the molybdenum is tieing up carbon as Mo_2C thereby denying carbon to the embrittling reaction.

The apparent correlation between the drop-off point of the transition temperature plateau and the inflection point on the hardness curves is of considerable interest. The correlation indicates quite clearly that secondary hardening does not cause increased embrittlement since the inflection point is the measurable start of the secondary hardness reaction and at this temperature the transition temperature is undergoing a rapid decrease

in severity. Again it appears that the role of molybdenum must be one of pirating essential elements away from the embrittling reaction. Further substantiation of this lack of correspondence between secondary hardening and embrittlement is the continuity of the transition temperature response in the tempering range corresponding to the secondary hardness peak. In contrast to the hardness peak, the transition temperature senses no unusual behavior. It proceeds in a positive continuous manner from the minimal point, which customarily follows "500 degree embrittlement," through the tempering region which produces the hardness peak and on into regions corresponding to overaged conditions.

It is interesting to note the strong effect that double tempering has on the transition temperature as compared to the negligible effect on hardness. This disparity in response suggests that the reactions taking place with longer tempering time at slightly reduced temperature are more in the nature of morphological changes rather than changes in bulk quantities. The increase in transition temperature with double tempering appears to obviate retained austenite as a cause. The actual response is diametrically opposite to the decrease in transition temperature which would normally have occurred if retained austenite were a significant contributor.

The effects of prior austenitic grain size on the transition temperature are also clearly illustrated in the data from the 2% Mo alloy. An increase of two and a half ASTM grain size numbers, or from ASTM 8 to ASTM 5-6, developed an approximate increase in the transition temperature of 100 Fahrenheit degrees. Utilizing the relationship of Heslop and Petch[18] and extrapolating their linear relationship to the grain sizes found in this investigation, the calculated increase in transition temperature is 120 Fahrenheit degrees for a shift from ASTM 8 to ASTM 5.5, and 100 Fahrenheit degrees for a shift from ASTM 8 to ASTM 6. This is considered to be in good agreement with the experimental data of this investigation. In addition to the vertical shift, there is also a horizontal shift in the embrittlement phenomena with changing grain size. For the larger austenitic grain size the location of the upper limit of the transition temperature plateau has been moved approximately 100 degrees to higher tempering temperatures.

Since the 2% Mo alloy is more embrittled at larger austenitic grain sizes, which is synonymous with having less grain boundary area, it would appear that the prior austenitic grain boundaries are not the prime site of embrittlement. The delay in the appearance of the drop-off from the plateau with increased austenitic grain size would then appear to derive from greater diffusion distances within the grains. Possibly the atoms of interest must

diffuse away from, rather than toward the prior austenitic grain boundaries. Further experimental work is necessary to substantiate the cause of the horizontal shift with increased grain size.

The heavy scatter in the transition temperature data for the 5% Mo alloy is believed to be primarily the result of undissolved carbides in the matrix. According to Bain and Paxton [9], plain carbon steel will dissolve five percent molybdenum at a maximum carbon solubility of approximately 0.43% and this at a temperature of 2250°F. These temperature and solubility limits are also coincident with the onset of liquation. Since the investigatory 5% Mo alloy was austenitized at 2075°F to avoid liquation, it is physically impossible for all of the molybdenum to go into solid solution in the austenite.

CONCLUSIONS

The following conclusions are based primarily on the experimental results from the 0% Mo and the 2% Mo alloys and are made with the assumption that the molybdenum was essentially in complete solid solution during the austenitizing treatment.

1. The heat treatment producing the maximum secondary hardness effect in molybdenum alloyed steels does not similarly produce the maximum embrittled state. In the tempering region surrounding the secondary hardness peak the transition temperature response remains continuous and generally at a level considerably below that developed at lower tempering temperatures.

2. The addition of 2% Mo to a plain 0.40 carbon steel delays the onset of temper brittleness as indicated by the shift in the minima of the transition temperature response to higher tempering temperatures.

3. The addition of 2% Mo to a plain 0.40 carbon steel extends the range of "500 degree embrittlement" to higher tempering temperatures. The extension is caused by the shift in the transition temperature plateau to higher tempering temperatures.

4. Additions of 2% Mo to the 0.40 carbon base alloy do not markedly reduce the severity of "500 degree embrittlement" as indicated by the lack of significant vertical shift at the transition temperature plateau.

5. In the 2% Mo alloy an increase in the prior austenitic grain size of two ASTM fracture grain size numbers raises the transition temperature approximately 75 Fahrenheit degrees, and shifts the plateau approximately 150 Fahrenheit degrees to higher tempering temperatures.

6. Double tempering markedly increases the severity of embrittlement at all tempering temperatures for the 2% Mo alloy. This is directly in opposition to the reaction normally expected in alloy steels which are double tempered to remove retained austenite.

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TABLE I

Chemical Composition of Alloys Investigated

Heat Ident. (Nom. % Mo)	Heat Number	Elements Analyzed (Weight %)											
		C	Mn	Mo	P	S	Si	Ni	Cr	W	V	Cu	Al
0% Mo	RIE 117	0.42	0.47	<0.01	0.015	0.019	0.41	0.03	<0.04	<0.02	<0.01	0.09	0.013
2% Mo	RIE 118	0.44	0.45	1.95	0.01	0.021	0.36	0.04	<0.04	<0.02	0.01	0.07	0.010
5% Mo	RIE 120	0.41	0.43	4.85	0.01	0.025	0.49	0.05	<0.04	<0.02	0.01	0.11	0.015

TABLE II

Compilation of Test Data for the 0% Mo Base Alloy

Tempering* Temperature (deg F)	Average** Cross Sect. Hardness (Rockwell C)	Fracture Grain Size (ASTM No.)	Charpy V-Notch Transition Temperature (deg F)		
			6 ft-lb Criteria	8 ft-lb Criteria	10 ft-lb Criteria
As Quenched	58.7	6	-	-	-
465	51.6	7	-95	-	-
605	45.1	6-7	-65	+70	+100
675	42.4	6	-220	-185	-110
745	39.6	7	-360†	-260	-205
810	35.2	5-6	-	-	-
900	31.6	6	-365†	-320	-280
1005	25.3	7	-280	-240	-220

*All specimens annealed at 1500 F 1 hr, furnace cooled to 900 F and then air cooled to room temperature; austenitized at 1540 F 1 hr, brine quenched, followed by liquid nitrogen quench with 10 min. hold at -320 F; tempered at indicated temperature 1 hr, brine quenched.

**Hardness specimens were rough machined Charpy impact bars 0.440" square in cross section, 2.25" long, sectioned at longitudinal midpoint after heat treatment.

†Temperatures below -320 F are extrapolated points.

TABLE III

Compilation of Test Data for the 2% Mo Alloy

Tempering Temperature (deg F)	Type* Hardness Specimen	Average Cross Sect. Hardness (Rockwell C)	Fracture Grain Size (ASTM No.)	Charpy V-Notch Transition Temperature (deg F)		
				6 ft-lb Criteria	8 ft-lb Criteria	10 ft-lb Criteria
Following specimens annealed at 1665 F 1 hr, furnace cooled to 900 F and then air cooled to room temperature; austenitized at 1645 F 1 hr, oil quenched, followed by liquid nitrogen quench with 10 min hold at -320 F; tempered at indicated temperature 1 hr, brine quenched.						
As Quenched	H	56.3	-	-	-	-
As Quenched	I	56.7	7-8	-	-	-
410	H	55.0	-	-	-	-
460	I	54.9	8	-220	-120	-25
600	I	53.0	9	-190	-110	-50
610	H	51.9	-	-	-	-
675	I	51.6	9	-220	-145	-95
700	H	49.6	-	-	-	-
740	I	49.6	7-8	-265	-200	-100
745	I	48.5	9	-190	-145	-80
765	I	48.2	7-8	-290	-240	-200
795	H	48.2	-	-	-	-
815	I	49.0	8-9	-	-330**	-240
900	I	48.1	8-9	-	-350**	-290
905	H	48.0	-	-	-	-
955	H	46.6	-	-	-	-
1005	H	46.5	-	-	-	-
1025	I	47.0	9	-370**	-290	-255
1055	H	46.9	-	-	-	-
1095	H	44.5	-	-	-	-
1150	I	41.9	8	-240	-195	-150
1185	H	33.2	-	-	-	-
1300	H	23.7	-	-	-	-
Following specimens annealed and austenitized as above but tempered at first indicated temperature 1 hr, brine quenched, followed by liquid nitrogen quench with 10 min hold at -320 F, plus retempering at second indicated temperature 1 hr, brine quenched.						
605+550	I	54.4	9	-35	-15	+90
800+750	I	47.8	9	-160	-95	-50
1025+975	I	48.3	8-9	-270	-215	-170
Following specimens annealed at 1665 F 1 hr, furnace cooled to 900 F and then air cooled to room temperature; austenitized at 2100 F 1 hr, oil quenched, followed by liquid nitrogen quench with 10 min hold at -320 F; tempered at indicated temperature 1 hr, brine quenched.						
670	I	52.1	5	-125	-50	+30
740	I	51.2	5-6	-165	-100	-5
835	I	48.3	5-6	-190	-80	+50
920	I	47.9	5	-270	-200	-125

*H = As-forged hexagonal cross-section 0.6" - 0.7" in diameter, approximately 2.25" long.
I = Rough machined Charpy impact bar, 0.440" square in cross section, 2.25" long.
**Transition temperatures below -320 F are extrapolated points.

TABLE IV

Compilation of Test Data for the 5% Mo Alloy

Tempering* Temperature (deg F)	Type** Hardness Specimen	Average Cross Sect. Hardness (Rockwell C)	Fracture Grain Size (ASTM No.)	Charpy V-Notch Transition Temperature (deg F)		
				6 ft-lb Criteria	8 ft-lb Criteria	10 ft-lb Criteria
Following specimens tempered at indicated temperature 1 hr, brine quenched.						
As Quenched	H	62.2	-	-	-	-
390	H	58.2	-	-	-	-
625	H	55.0	-	-	-	-
690	I	55.3	5	+40	+150	-
765	I	55.2	5	-20	-	-
780	I	55.3	4-5	+25	+250	-
810	H	53.8	-	-	-	-
855	I	54.6	5	-60	+10	+280
900	H	54.8	-	-	-	-
920	I	55.5	5	+20	+150	+300
1000	I	56.3	5	-40	+45	+160
1005	H	56.0	-	-	-	-
1035	H	58.1	-	-	-	-
1095	H	59.3	-	-	-	-
1145	H	54.8	-	-	-	-
1250	H	42.5	-	-	-	-
Following specimen tempered at first indicated temperature 1 hr, brine quenched, followed by liquid nitrogen quench with 10 min hold at -320 F; plus retempering at second indicated temperature 1 hr, brine quenched.						
920+860	I	56.3	4	+30	+140	-

*All specimens annealed at 2150 F 1 hr, furnace cooled to 900 F, and then air cooled to room temperature; austenitized at 2075 F 1 hr, oil quenched, followed by liquid nitrogen quench with 10 min hold at -320 F.

**H = As-forged hexagonal cross-section 0.6" - 0.7" in diameter, approximately 2.25" long.

I = Rough machined Charpy impact bar, 0.440" in cross section, 2.25" long.

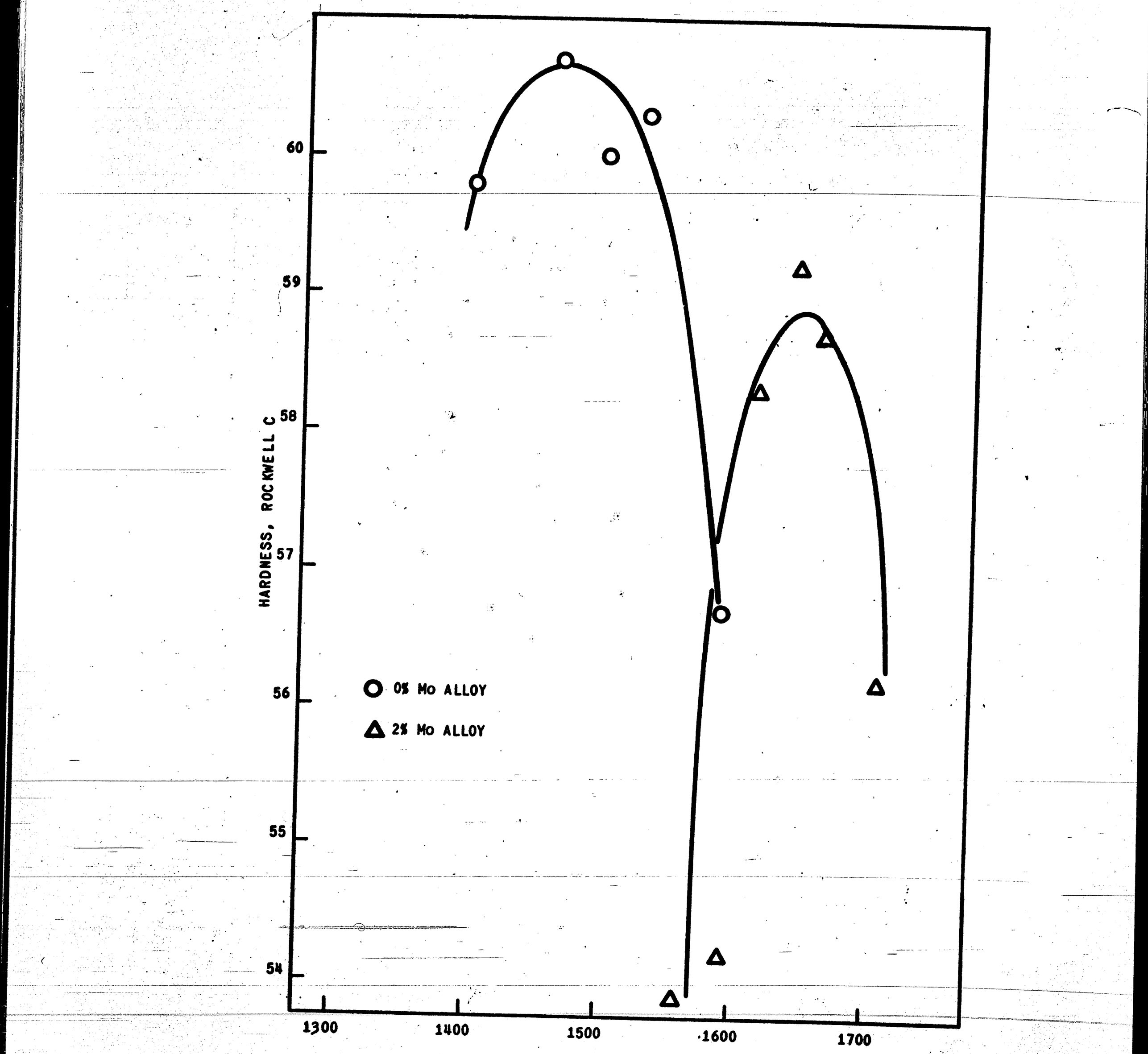

Figure 1. EFFECT OF AUSTENITIZING TEMPERATURE ON AS-QUENCHED HARDNESS FOR THE 0% AND 2% Mo ALLOYS

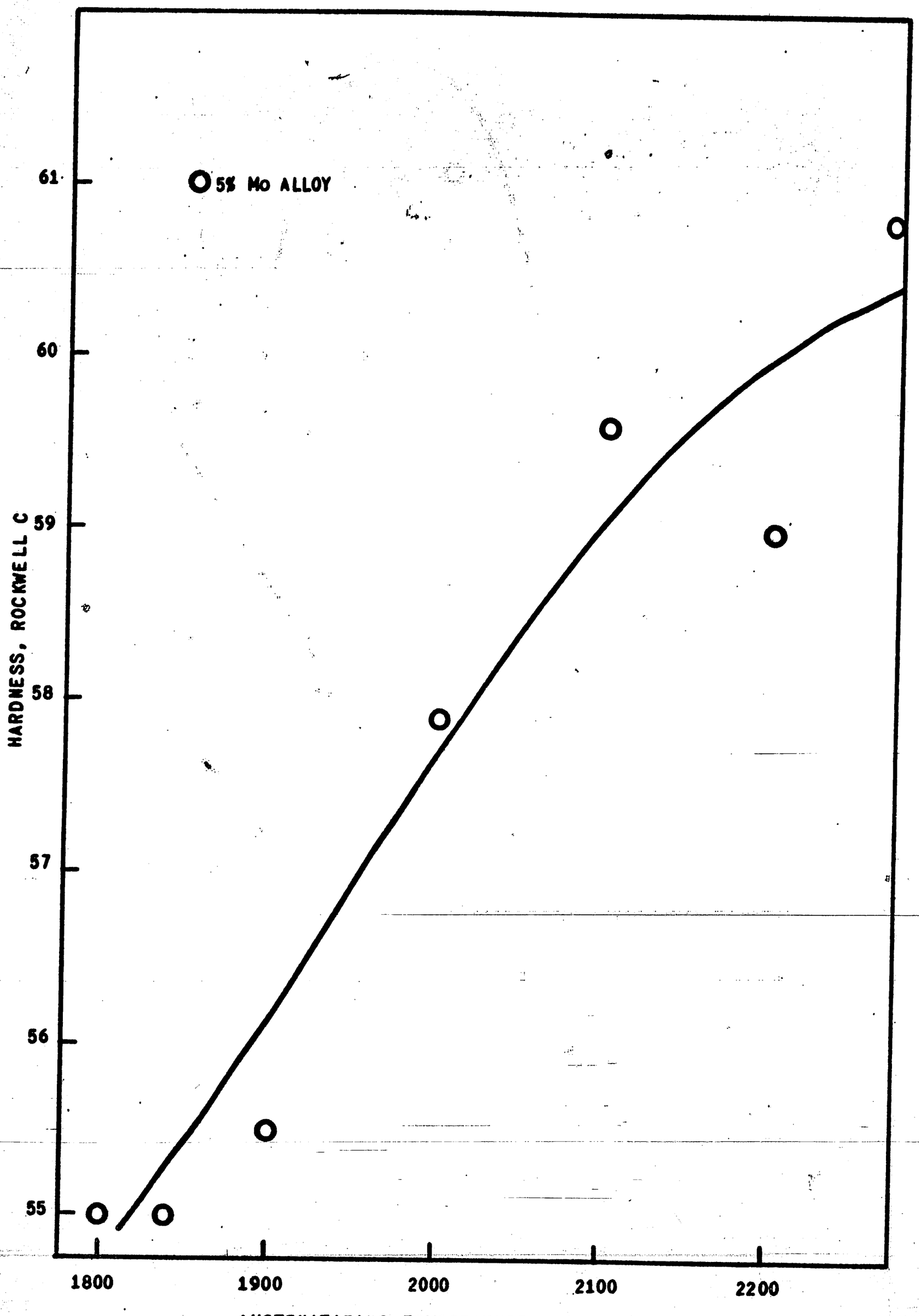

Figure 2. EFFECT OF AUSTENITIZING TEMPERATURE ON AS-QUENCHED HARDNESS FOR THE 5% Mo ALLOY

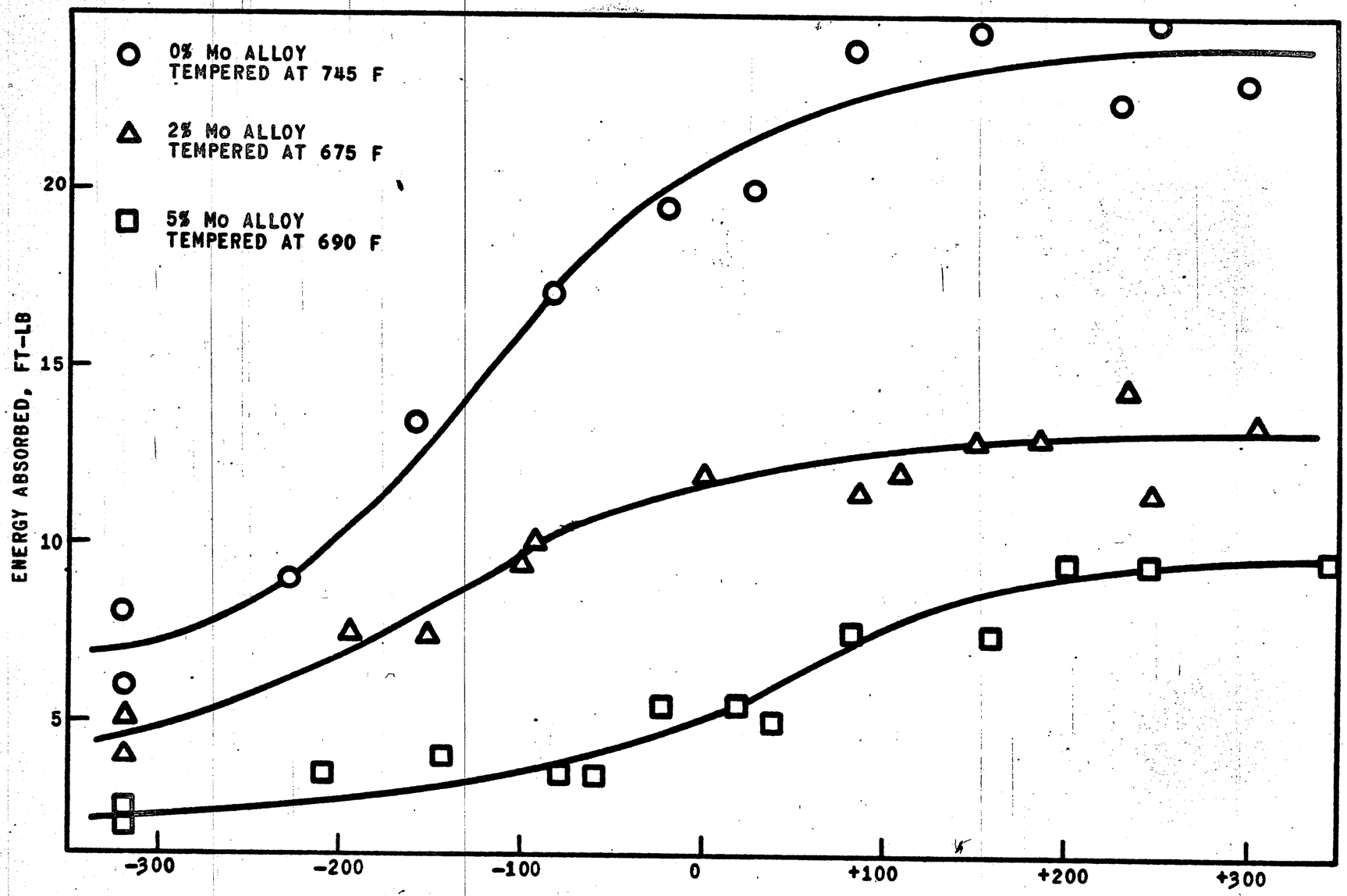

Figure 3. TYPICAL IMPACT ENERGY BEHAVIOR OF THE 0%, 2%, AND 5% Mo ALLOYS AS INFLUENCED BY TESTING TEMPERATURE

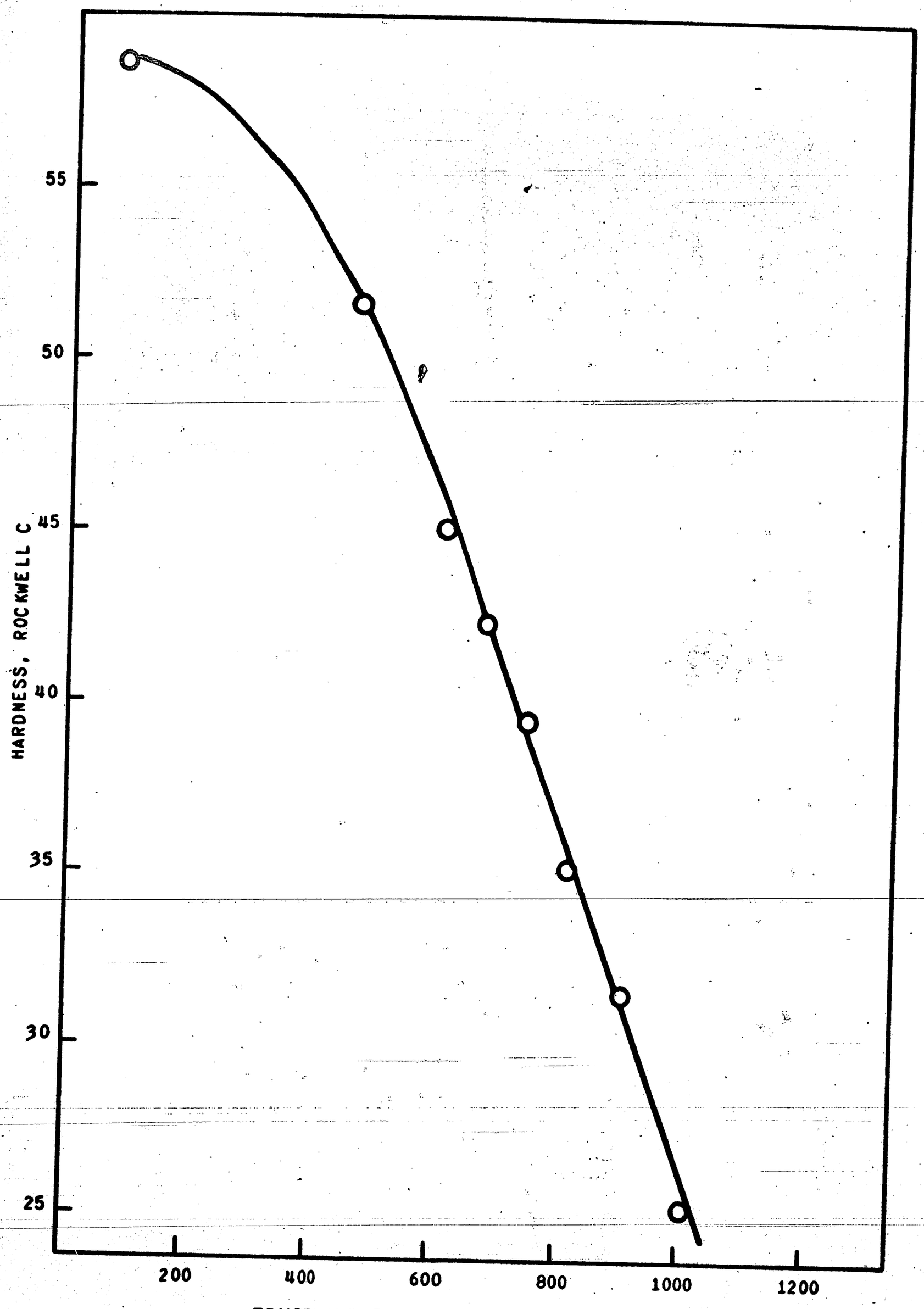

Figure 4. EFFECT OF TEMPERING TEMPERATURE ON THE HARDNESS OF THE 0% Mo ALLOY

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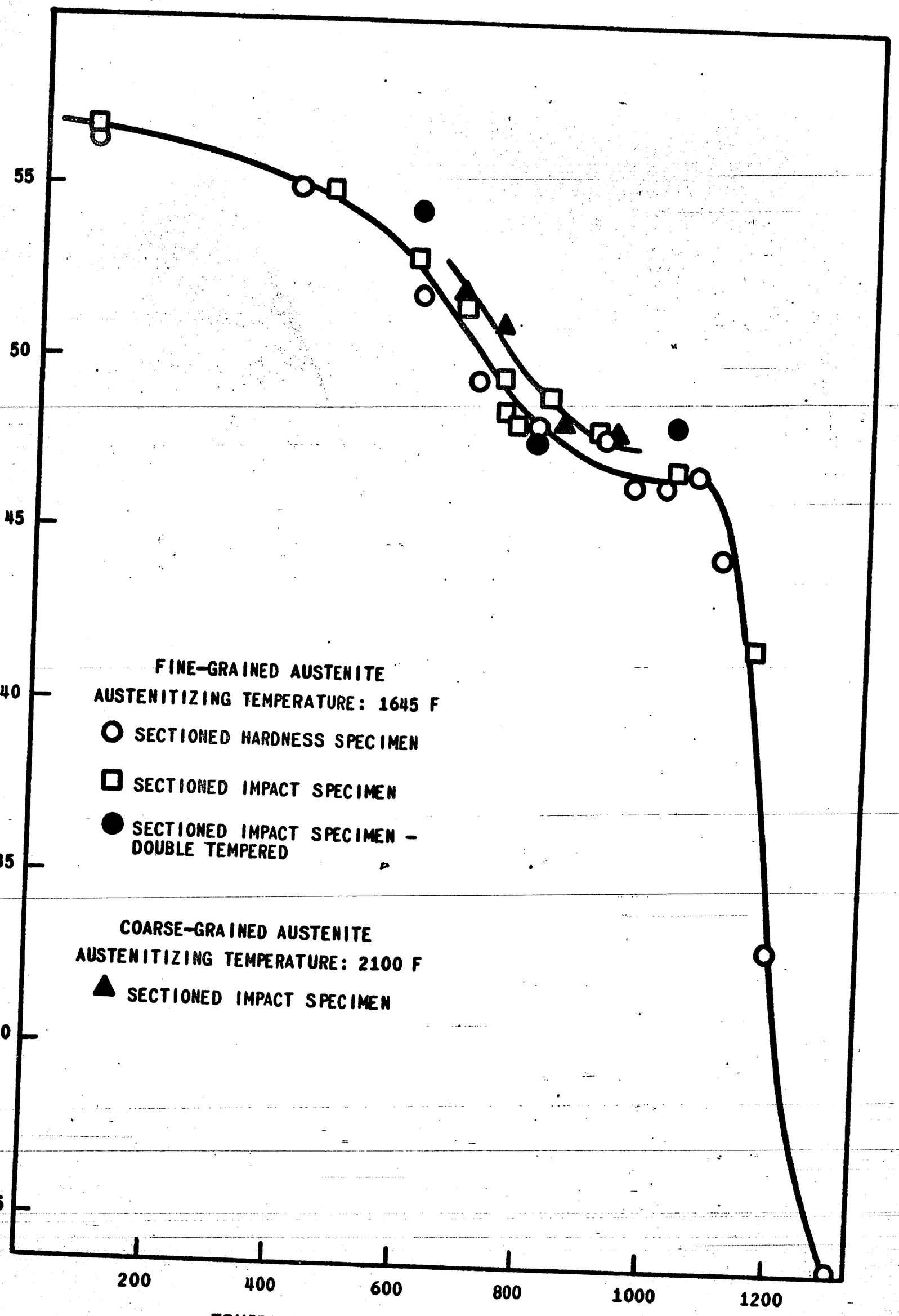


Figure 5. EFFECT OF TEMPERING TEMPERATURE ON THE HARDNESS OF THE 2% Mo ALLOY

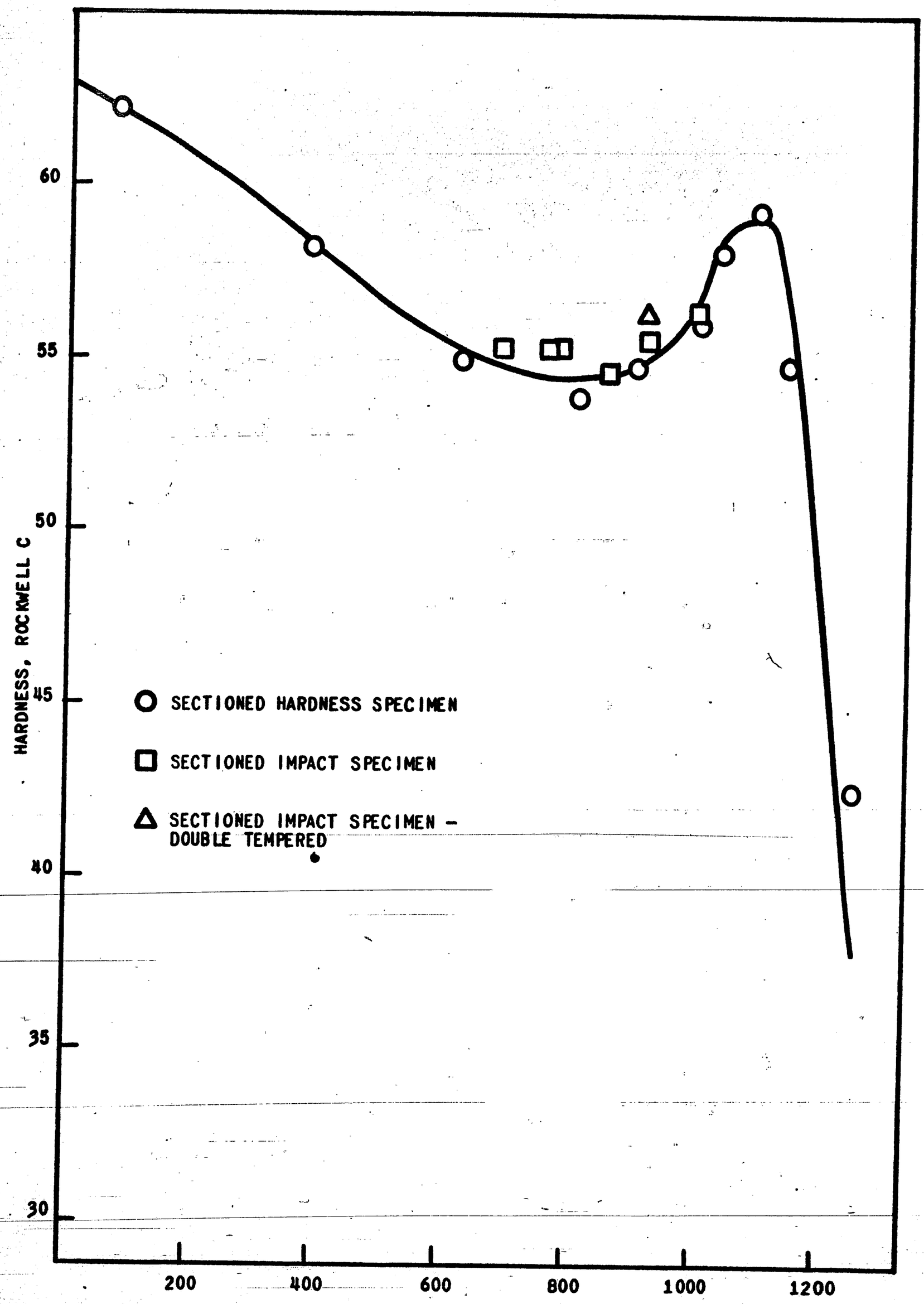


Figure 6. EFFECT OF TEMPERING TEMPERATURE ON THE HARDNESS OF THE 5% Mo ALLOY

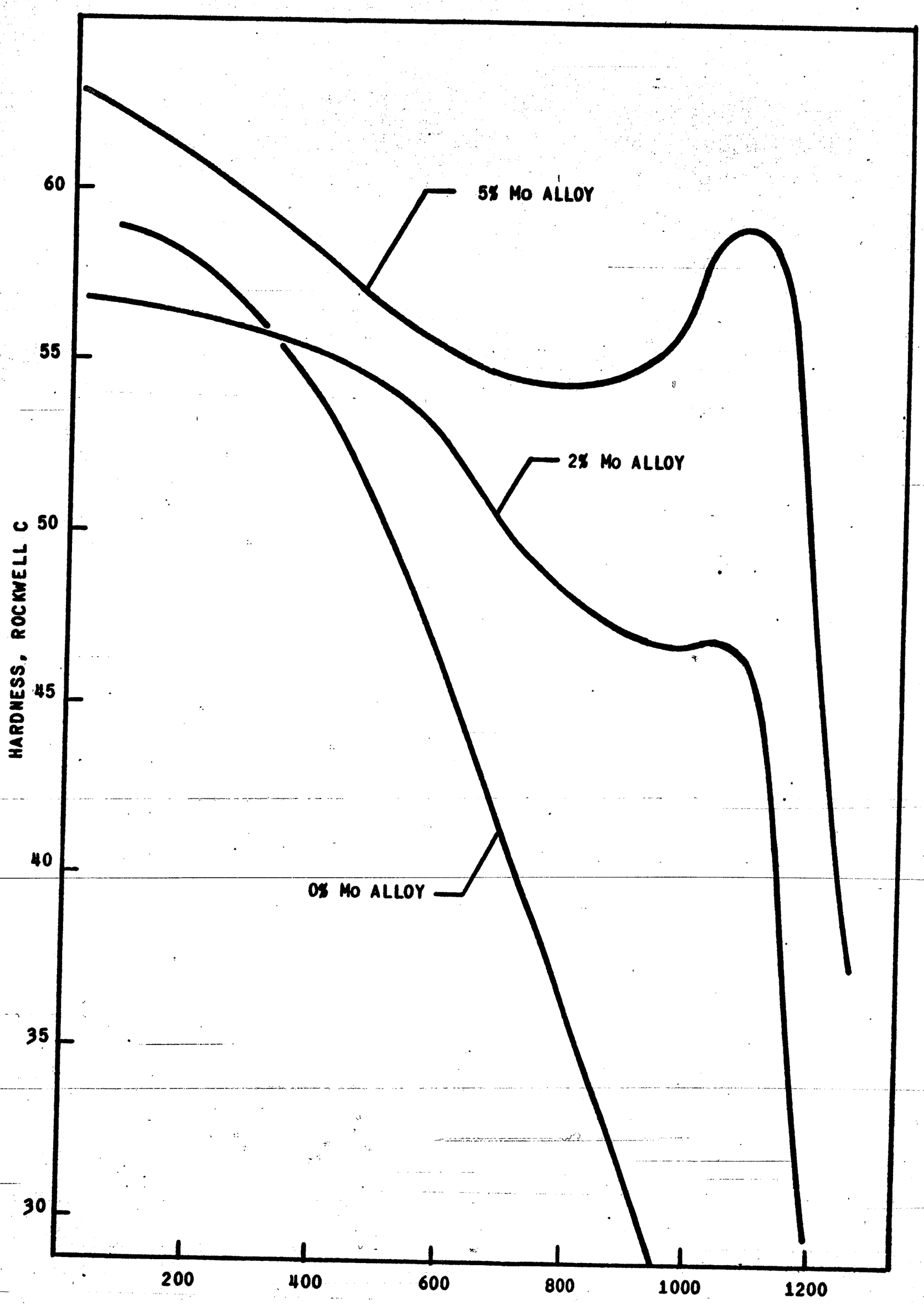


Figure 7. COMPARISON ON THE EFFECT OF TEMPERING TEMPERATURE ON THE HARDNESS OF THE 0%, 2%, AND 5% Mo ALLOYS

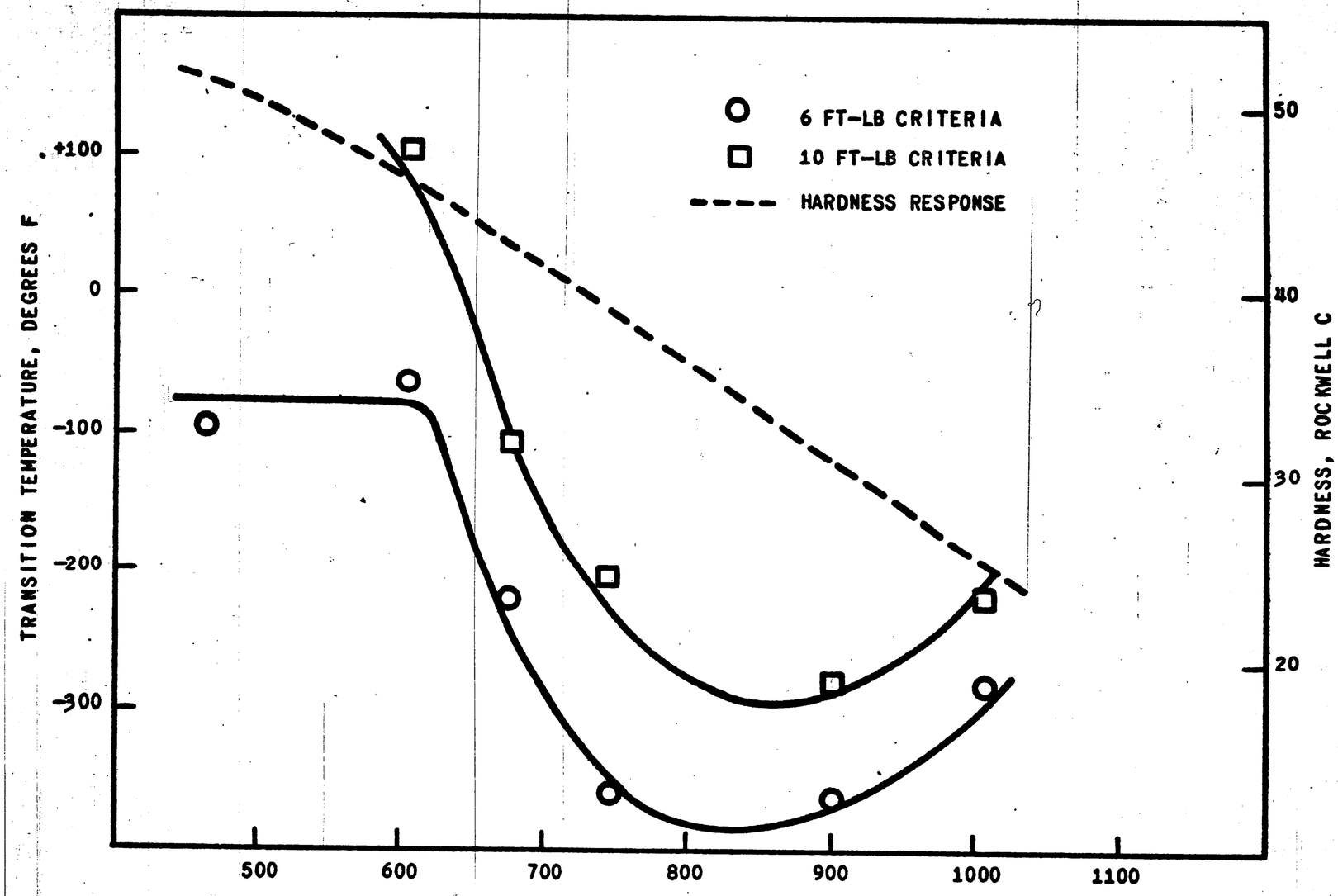


Figure 8. EFFECT OF TEMPERING TEMPERATURE ON THE TRANSITION TEMPERATURE AND HARDNESS OF THE 0% Mo ALLOY

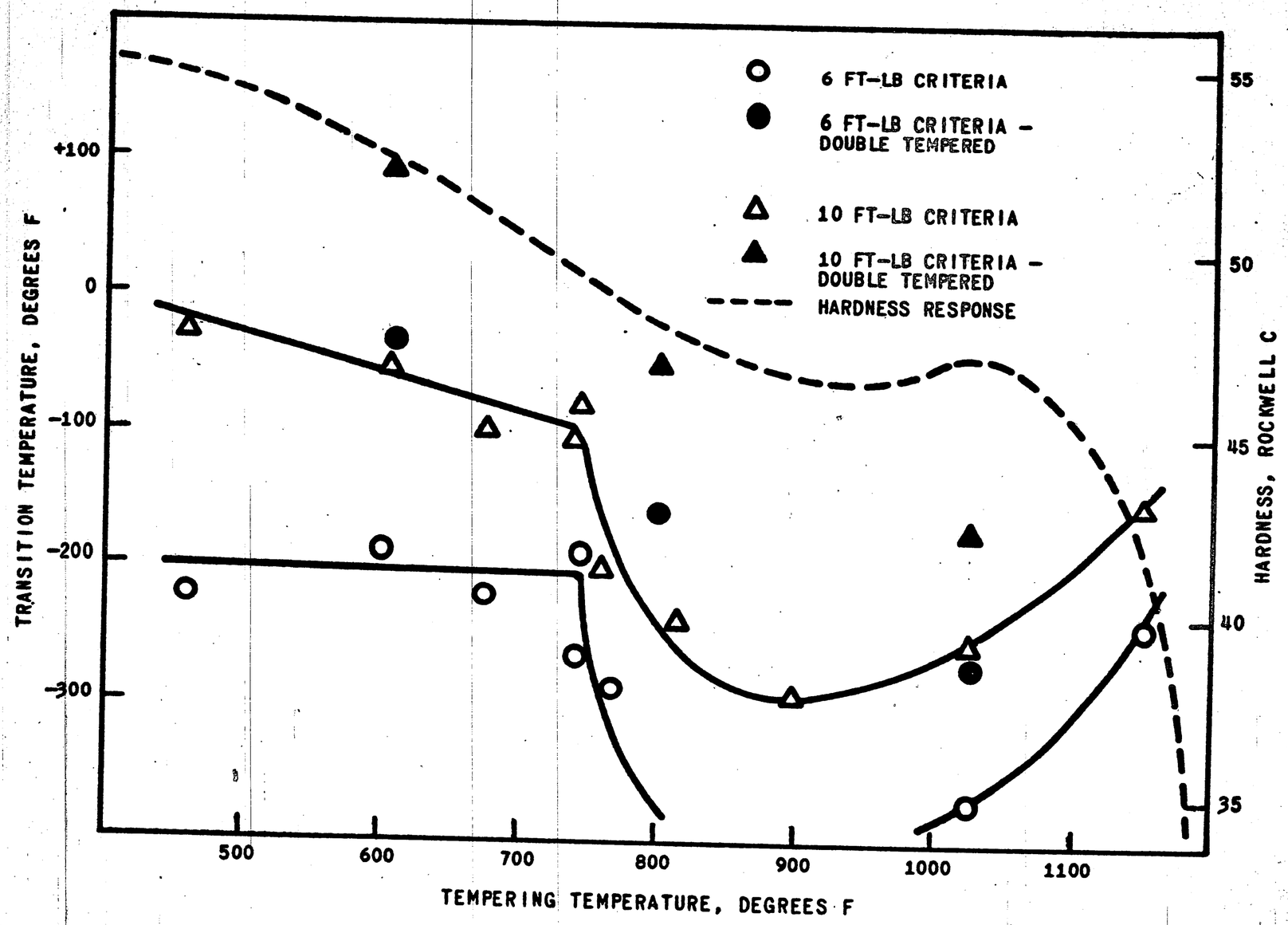


Figure 9. EFFECT OF TEMPERING TEMPERATURE ON THE TRANSITION TEMPERATURE AND HARDNESS OF THE 2% Mo ALLOY AUSTENITIZED AT 1645 F

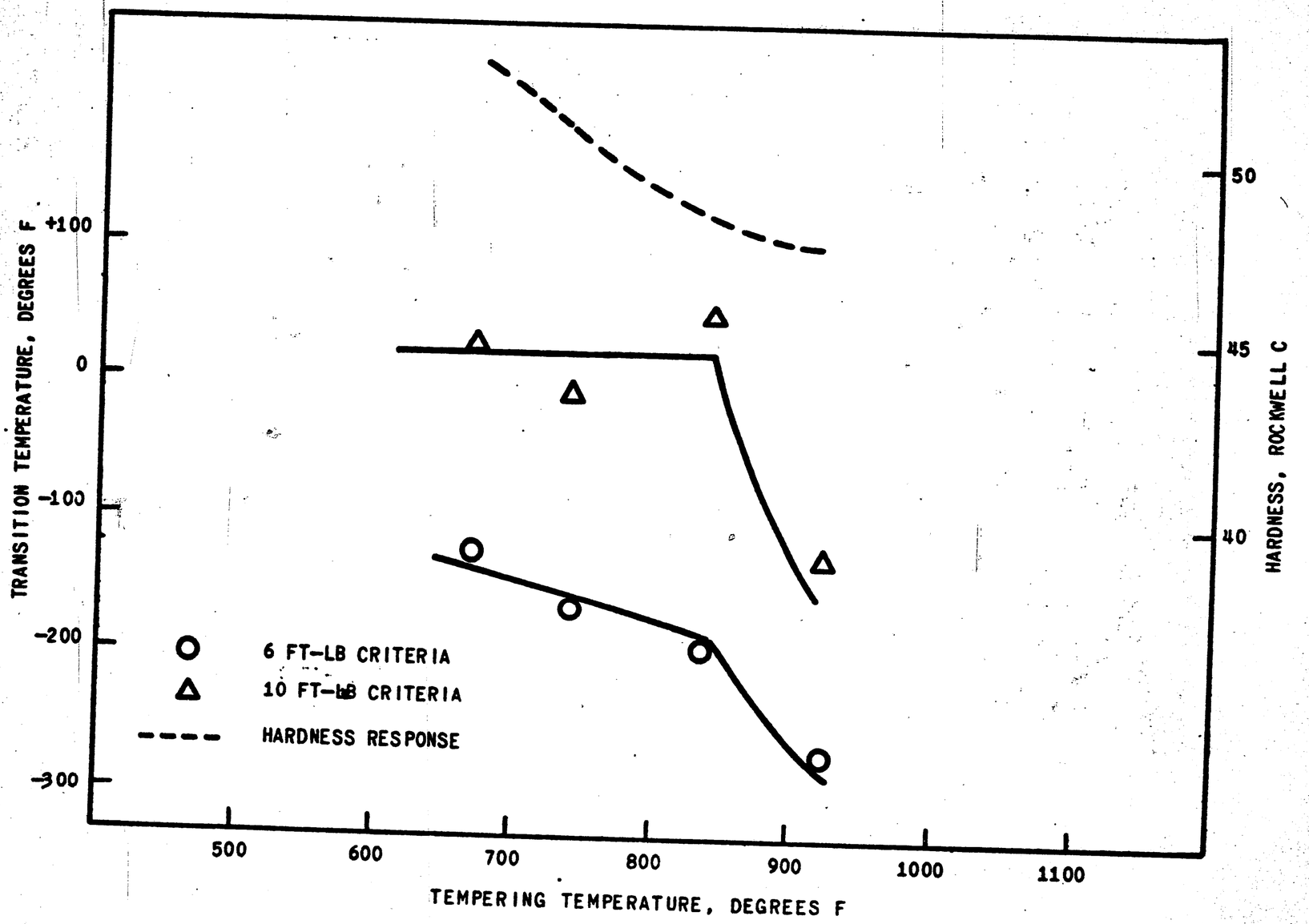


Figure 10. EFFECT OF TEMPERING TEMPERATURE ON THE TRANSITION TEMPERATURE AND HARDNESS OF THE 2% Mo ALLOY AUSTENITIZED AT 2100 F

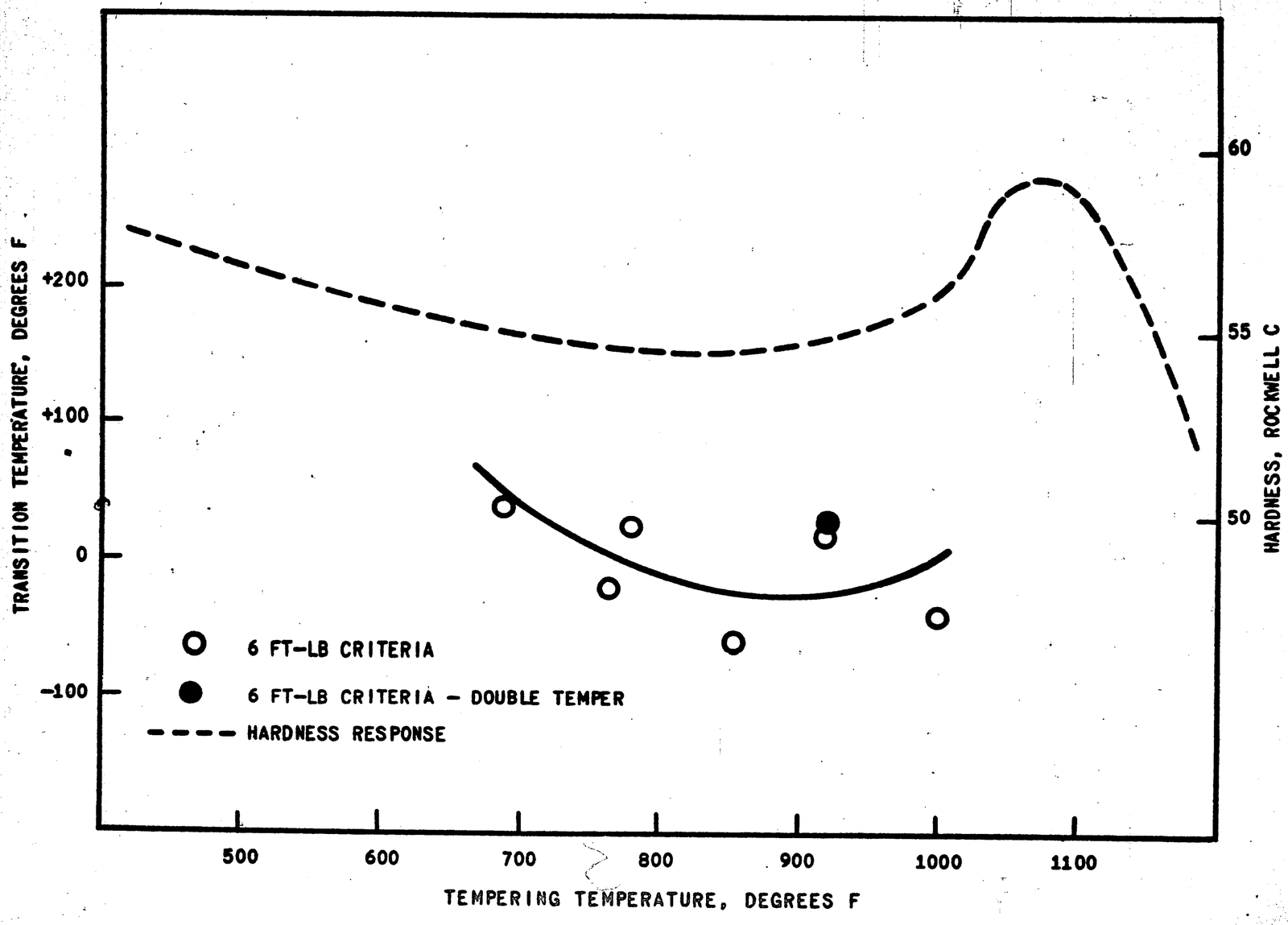


Figure 11. EFFECT OF TEMPERING TEMPERATURE ON THE TRANSITION TEMPERATURE AND HARDNESS OF THE 5% Mo ALLOY

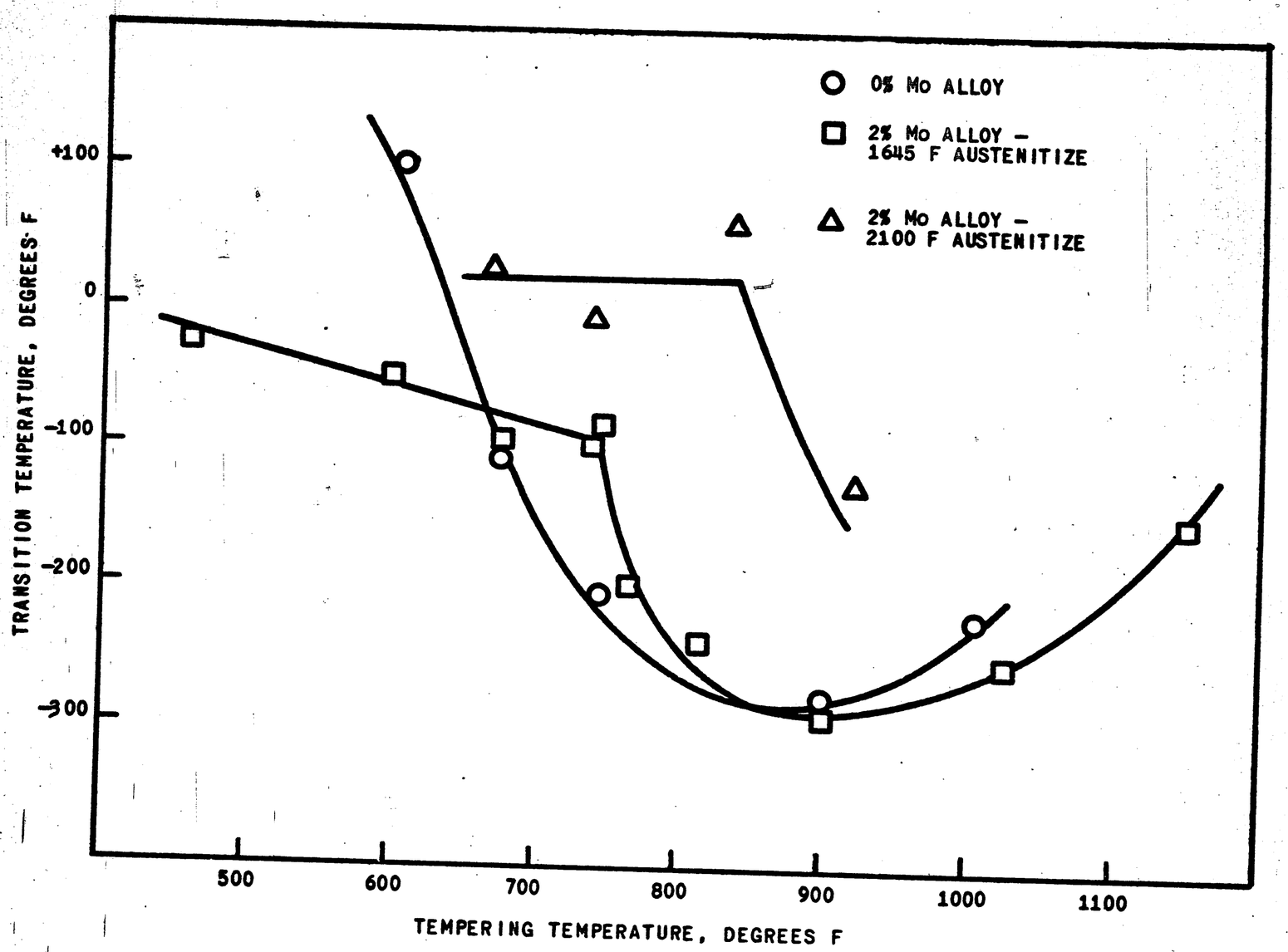


Figure 12. EFFECT OF TEMPERING TEMPERATURE ON THE 10 FT-LB TRANSITION TEMPERATURE OF THE 0% AND 2% Mo ALLOYS

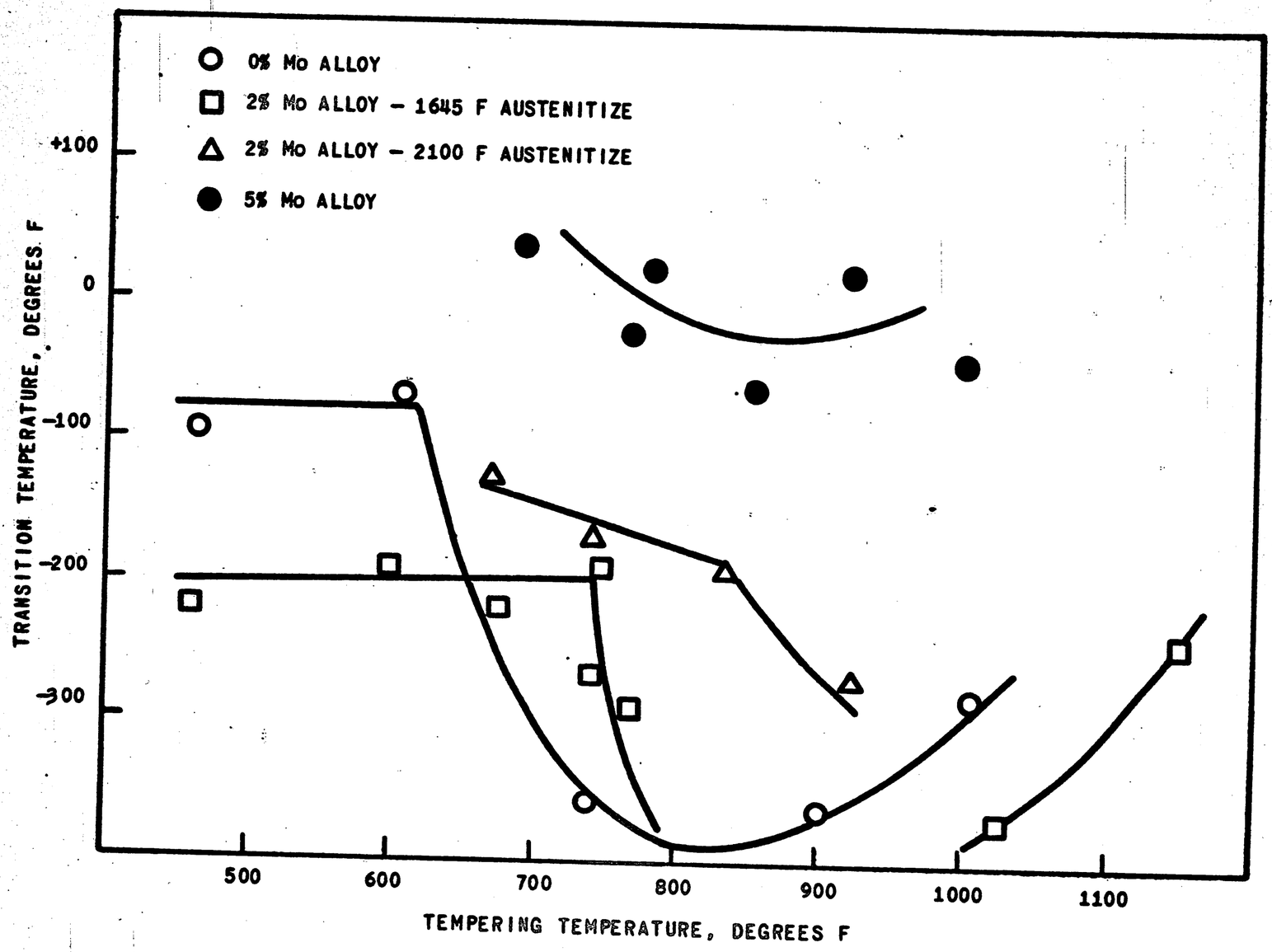
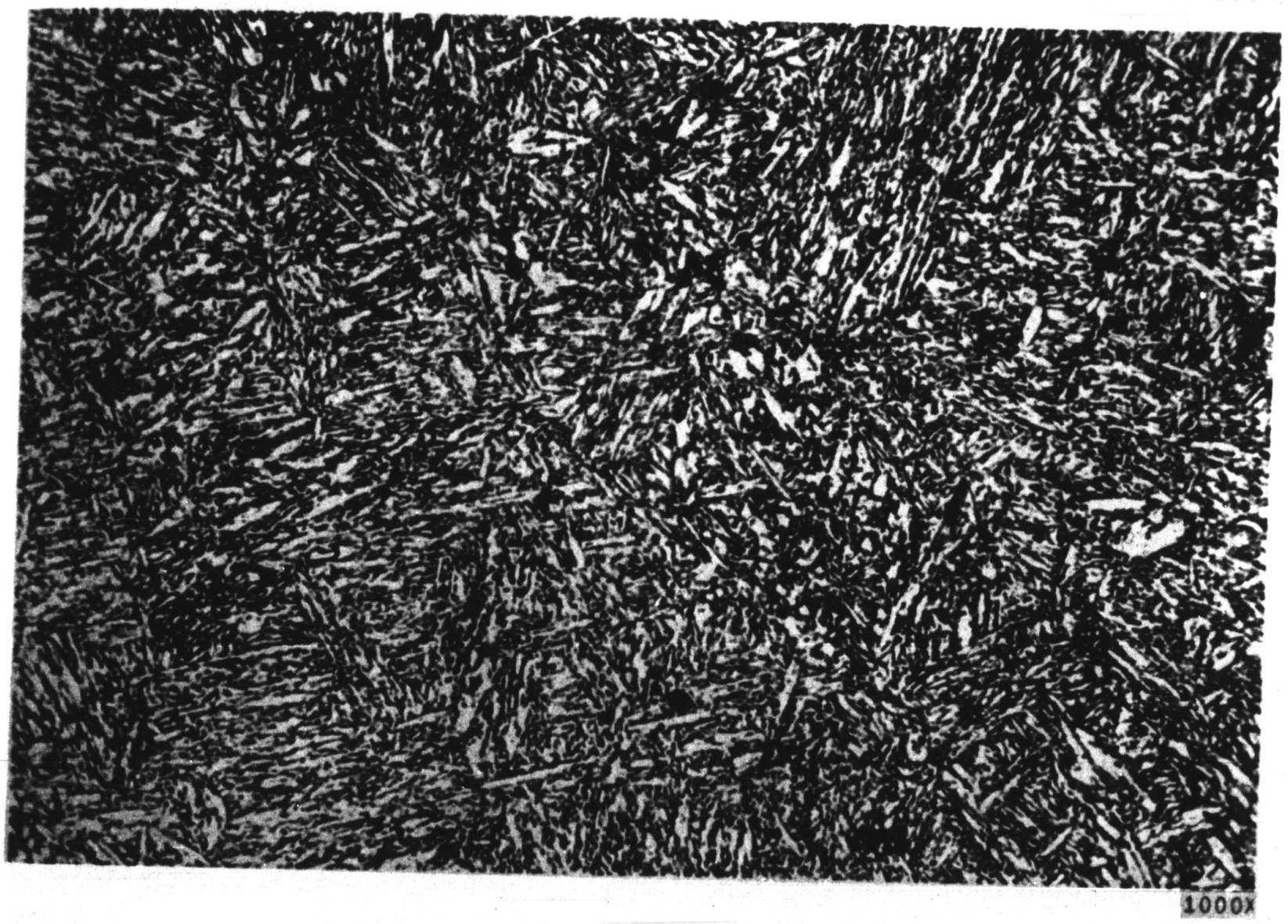


Figure 13. EFFECT OF TEMPERING TEMPERATURE ON THE 6 FT-LB TRANSITION TEMPERATURE OF THE 0%, 2% AND 5% Mo ALLOYS

100X



1000X

Figure 14. TYPICAL MICROSTRUCTURE OF THE 0% Mo BASE ALLOY IN THE QUENCHED AND TEMPERED CONDITION. ABOVE SAMPLE AUSTENITIZED AT 1540 F FOR 1 HOUR AND TEMPERED AT 675 F FOR 1 HOUR. (Etchant: 1% Nital)

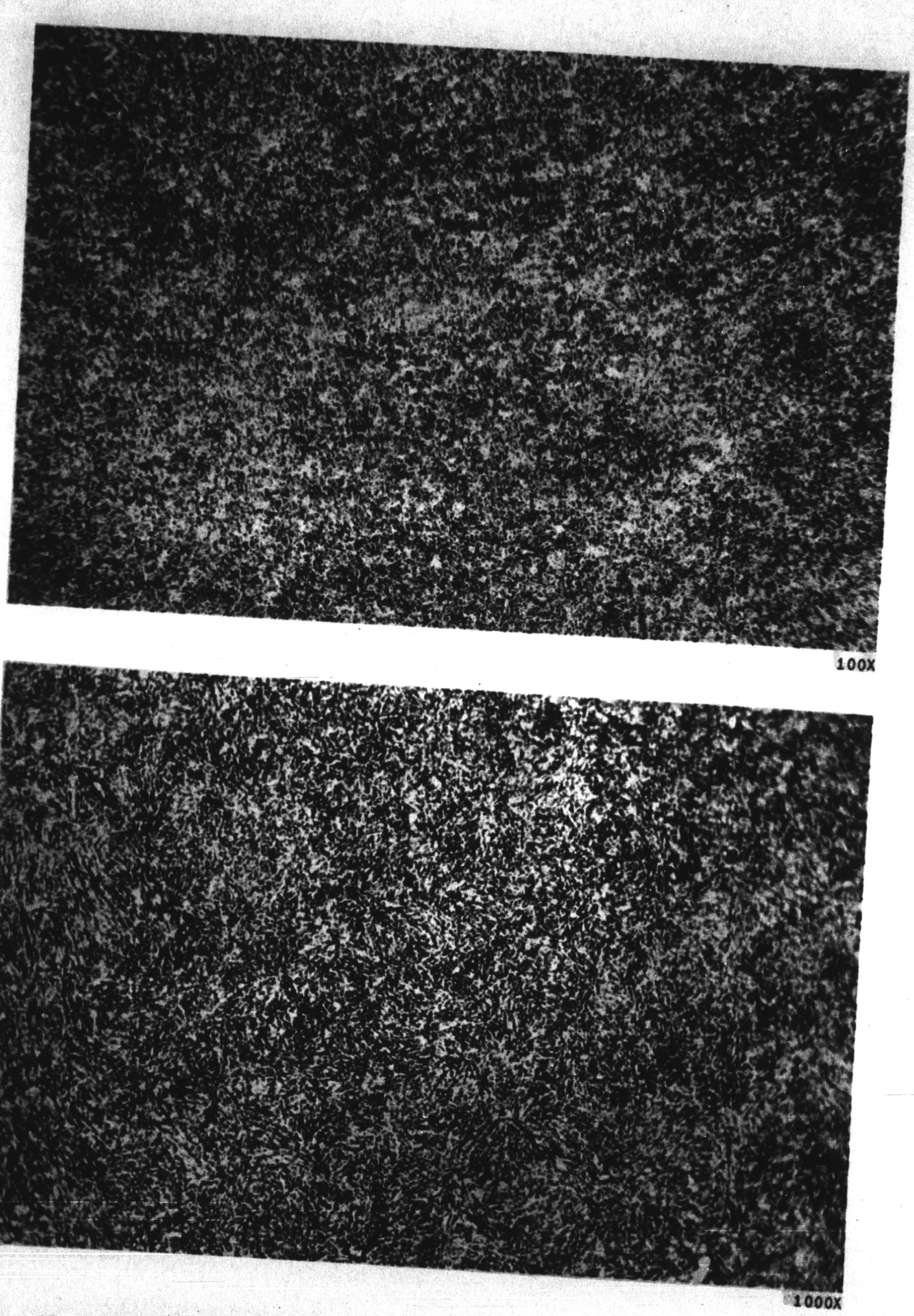


Figure 15. TYPICAL MICROSTRUCTURE OF THE FINE-GRAINED 2% Mo ALLOY IN THE QUENCHED AND TEMPERED CONDITION. ABOVE SAMPLE AUSTENITIZED AT 1645 F FOR 1 HOUR AND TEMPERED AT 745 F FOR 1 HOUR. (Etchant: 1% Nital)

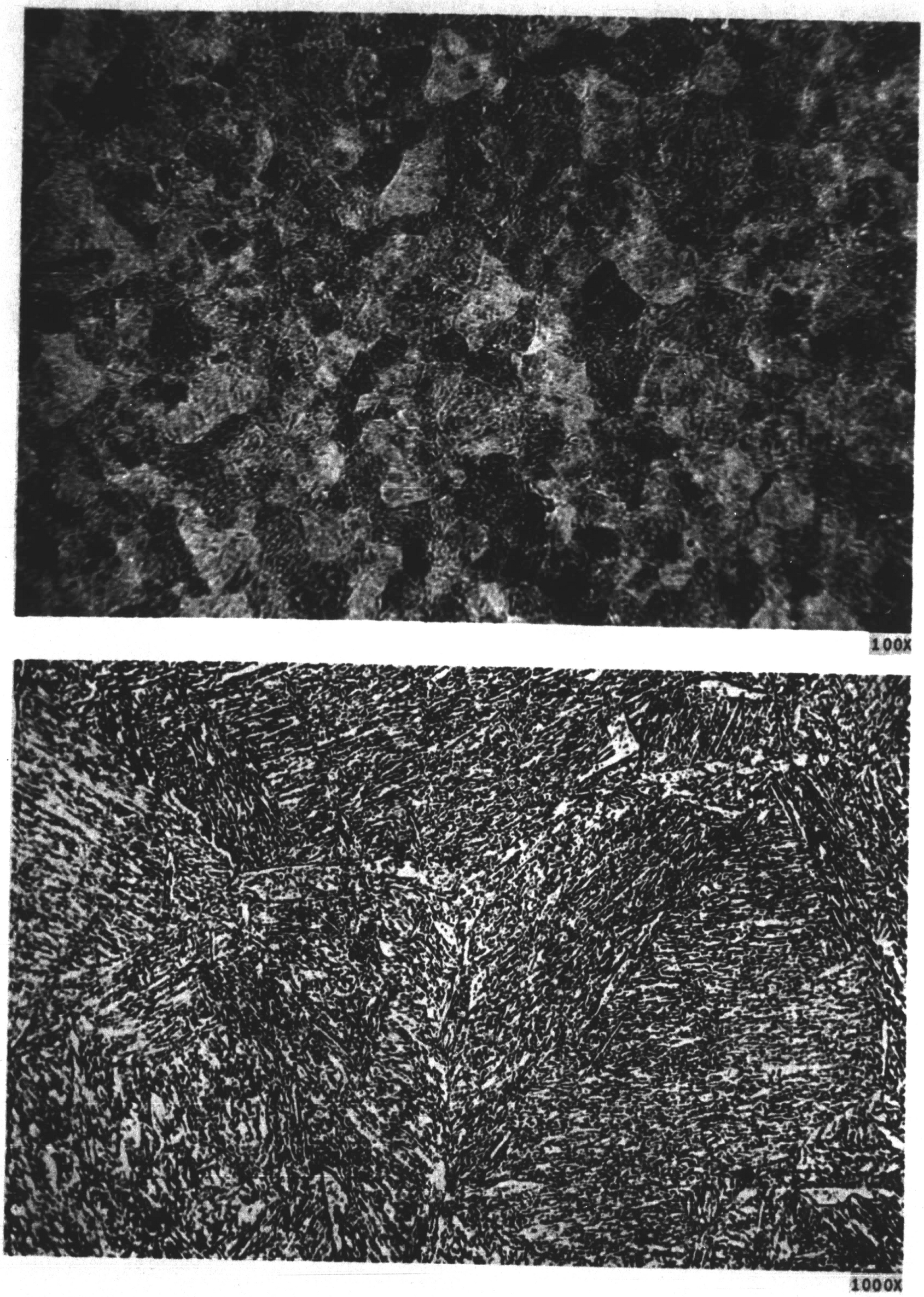
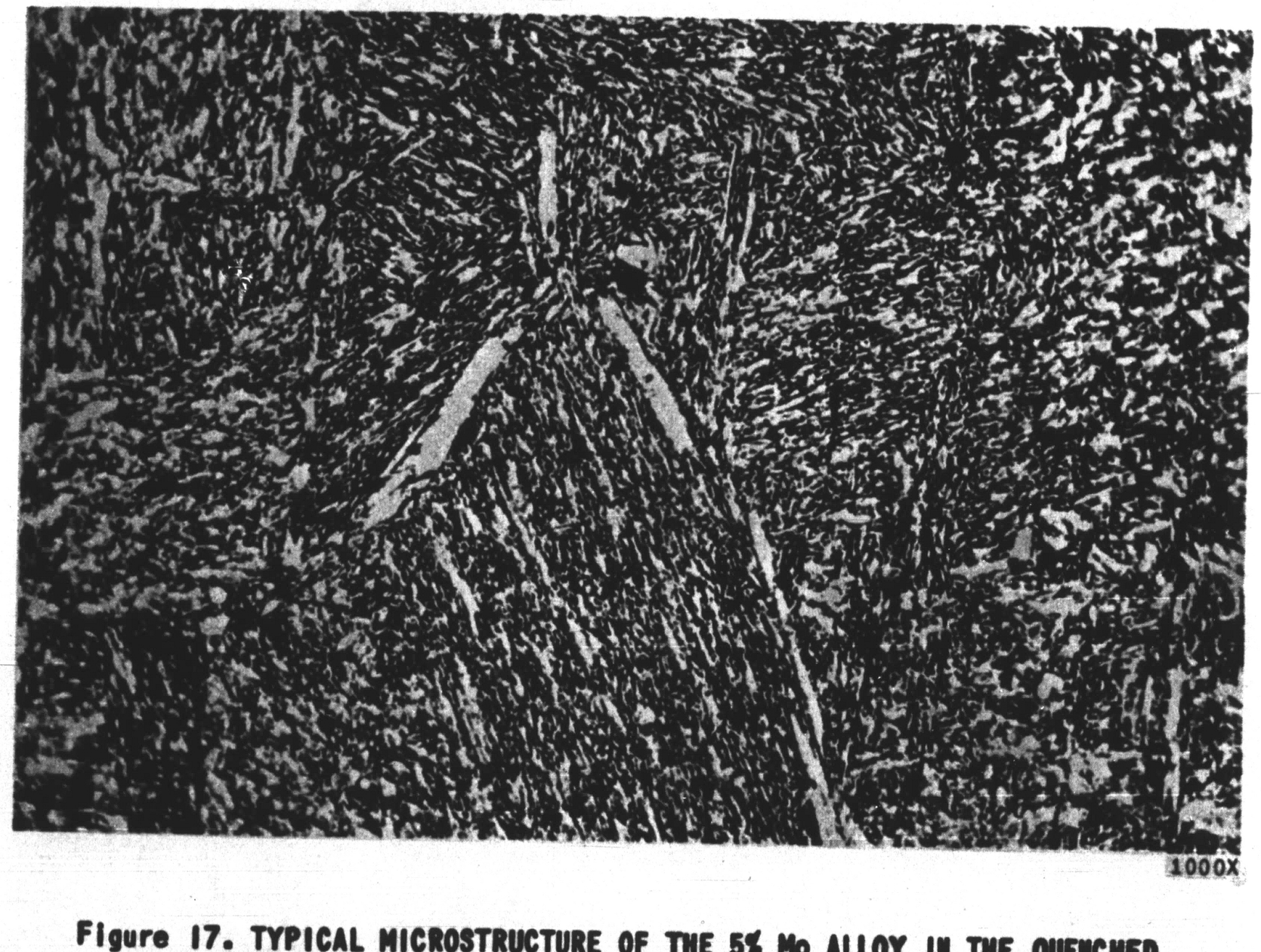


Figure 16. TYPICAL MICROSTRUCTURE OF THE COARSE-GRAINED 2% Mo ALLOY IN THE QUENCHED AND TEMPERED CONDITION. ABOVE SAMPLE AUSTENITIZED AT 2100 F FOR 1 HOUR AND TEMPERED AT 835 F FOR 1 HOUR. (Etchant: 1% Nital)

100X



1000X

Figure 17. TYPICAL MICROSTRUCTURE OF THE 5% Mo ALLOY IN THE QUENCHED AND TEMPERED CONDITION. ABOVE SAMPLE AUSTENITIZED AT 2075 F FOR 1 HOUR AND TEMPERED AT 1000 F FOR 1 HOUR. (Etchant: 1% Nital)

VITA

Edward Everett Chick, the son of Mr. and Mrs. Ralph E. Chick of Portsmouth, New Hampshire, was born on 13 June 1931 in Bangor, Maine. He received his elementary and high school education in the Claremont, New Hampshire school system, graduating therefrom in June 1949. He entered Lehigh University in the fall of 1949 and graduated four years later with a Bachelor of Science Degree in Metallurgical Engineering. Upon graduation he was commissioned as a Second Lieutenant, USAR from ROTC (DMG). Following a two year tour of active duty with the Ordnance Corps he returned to civilian life and was employed by Giffels, Vallet, and Rossetti, a consulting engineering firm in Detroit, Michigan. Two years later he accepted a position as Technical Engineer with the Aircraft Gas Turbine Division, General Electric Company, Cincinnati, Ohio. In March 1959 he accepted a commission in the Regular Army direct from civil life and returned to active duty as a First Lieutenant spending a two year combat arms tour with the Artillery at Fort Sill, Oklahoma. In June 1961 he was returned to the control of the Ordnance Corps and stationed at Lehigh University for graduate studies leading to the degree of Master of Science in Metallurgical Engineering. Captain Chick is married to the former Jouette Eifert of Reading, Pennsylvania. Captain and Mrs. Chick are the parents of three children.